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THEORY AND PRACTICE OF ELECTRO-DEPOSITION,

BY

Dr. G. GORE, F. R. S.

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MEDICAL
DR. H. C.

ELECTRO-DEPOSITING ROOM.

ELECTRO-METALLURGY.

THE THEORY OF ELECTRO-DEPOSITION.

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THEORY AND PRACTICE

—OF—

ELECTRO-DEPOSITION,

INCLUDING EVERY KNOWN MODE OF

Depositing Metals, Preparing Metals for Immersion, Taking Moulds and Rendering them Conducting.

BY

DR. G. GORE, F.R.S.

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1888.

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PREFACE.

THIS little book was originally written in the year 1856, ever since which time it has had an extensive and continuous sale, both in this country and in America, and has been especially used by large numbers of working electro-platers in manufactories of electro-plated articles.

As during the last few years the process of electro-plating has been somewhat modified by the development of the dynamo-electric-machine, it has been considered desirable to make some additions to, and alterations in, the original text, so as to maintain the value and suitability of the book for the class of readers for whom it was originally written. With that view, the desired additions and alterations have been made by a competent authority on the subject. The chief additions will be found on pages 37–38, respecting the thermic relations of electrolysis, and on pages 44 to 55, relating to dynamo-electric machines. Several useful tables have also been added at the end of the book.

ELECTRO-DEPOSITING ROOM.

ELECTRO-METALLURGY.

THE THEORY OF ELECTRO-DEPOSITION.

Introductory Remarks.—As the ultimate object of this treatise is to enable the reader to work in an electroplate manufactory in a commercially successful manner, we shall endeavour to include within its pages, as far as the limited space will allow, every portion of the subject calculated to assist him in obtaining that result, excluding from it every other portion which does not contribute towards that object.

With this view we shall include the *principles* or *theory* of electro-deposition, because every workman in an electroplate manufactory is certain to meet with difficulties, which no amount of practical knowledge or experience will enable him to overcome without a perfect knowledge of the theoretical principles. These difficulties may be new ones, such probably as he has never seen before, and no doubt, in some cases, such as no one else has ever seen; a knowledge of the theory will here enable him to apply its principles to the difficulties, and suggest remedies, some of which are almost sure to be successful. We shall also include the *practice* of the subject; because, after all,

success depends on careful manipulation; for with ever so complete a knowledge of principles, without a perfect knowledge of the application of those principles in the form of practical rules and practical manipulation, success cannot possibly be attained. With the same end in view, we shall avoid saying anything about the history of the subject, or the claims of rival discoverers or inventors, these being subjects for the historian. Neither shall we say much about the electro-deposition of rare metals, or about any collateral branches of the subject, excepting only so far as they are capable of illustrating the subject in a direct manner, or of otherwise furthering the object in view.

To enable the reader to master each portion of the subject as he proceeds, we have so arranged it that every portion shall be, so far as it goes, complete in itself, requiring no anticipatory knowledge of more advanced parts to enable him to understand it.

The only arrangement of the subject which admits of this important object being attained, is to treat of the theory before treating of the practice, and by arranging the theory in an *inductive* order. In other words, we shall commence with the various classes of facts on which the electro-deposition is founded, and ascend from these to the general laws or principles, chemical or electrical, which govern them. Proceeding from the theory to the practice, arranging all in a *deductive* order, and applying theoretical principles in the form of practical rules, the results cannot be other than successful. Beginning with the more general rules which apply to all electro-deposition processes, and to the electro-deposition of all metals, and proceeding, step by step, to those more special rules of manipulation which are required for the working of particular metals and solutions, the necessary acquirements for the production of the more difficult substances and more complicated works of art will be attained. Through the whole treatise, the reader will thus be led gradually from the most common and well-known facts to the most complex and difficult applications of electro-deposition.

In accordance with this plan, we will commence with a statement of such facts of electro-deposition as every man possessing the few necessary materials, which are easily procurable, may readily verify for himself. On these facts the whole subject throughout will be based. From them we shall proceed to the circumstances or *conditions* under which they occur, namely, the *causes* of electro-deposition. The principles will be inferred from the facts as we proceed, until we arrive at the more abstract conditions of the phenomena.

The facts will be based on numerous experiments, in which instances where deposition does occur, as well as experiments in which it does not occur, will be cited. These investigations will satisfy the

reader that in all cases where deposition does occur, certain conditions are invariably present; and where it does not occur, one or more of those conditions is invariably absent; and therefore, that the conditions observed are the causes of the phenomena. Another and more ultimate reason for mentioning negative as well as positive instances is, that in practical working it is nearly as important to know what will prevent deposition, as to know what will produce it.

The following table exhibits the phenomena of electro-deposition arranged in an inductive order, suitable for learning the subject theoretically, and without immediate reference to its practical applications. The first portion of the table contains the *facts* of electro-deposition, divided into seven classes, under which may be ranged the whole known facts of the science. The second portion contains the *principles* or *conditions* under which those facts are manifested; these are also divided into seven classes, which are capable of including all the known conditions or causes of electro-deposition.

A.—FACTS.

1. Deposition by one metal and one liquid.
2. Deposition by two metals and one liquid.
3. Deposition by one metal and two liquids.
4. Deposition by two metals and two liquids.
5. Deposition by connecting either of the foregoing arrangements (except the first) with a separate depositing liquid.
6. Deposition by connecting other sources of depositing power with a separate depositing liquid.
7. Deposition by combinations of the foregoing.

B.—PRINCIPLES.

1. Chemical conditions of deposition.
2. Electrical conditions of deposition.
3. Thermic conditions of deposition.
4. Mechanical conditions of deposition.
5. Mathematical conditions of deposition.
6. Logical conditions of deposition.
7. Ontological conditions of deposition.

This arrangement has been used with much success in teaching the theoretical part of electro-deposition, enabling the pupils to understand each portion clearly as they proceeded. The plan adopted was—

First, to exhibit before the pupils numerous experiments of each class of facts in succession, including positive cases in which deposition did occur, as well as negative ones in which it did not occur.

Second, to place each of the theoretical principles in succession before them in the form of a hypothetical question, referring them to the various facts on which it is founded, and leaving them to observe

for themselves whether or not the principle there stated was borne out, allowing them to draw their own conclusions. By this method they were soon led to observe, that, wherever deposition occurred, certain conditions were present, and that where it did not occur those conditions were absent.

When treating of the laws and principles of deposition, the reader will be referred back to the facts upon which they are based; so, when describing its practical applications, he will in like manner be referred to the laws or principles for his guidance; his knowledge of the practice will thus be based in a great measure upon the principles, and the principles will be deduced from the facts, which, as we have said before, are within the reach of every one to repeat and prove for himself.

The practical part will treat in succession of the general rules for working all the different processes of washing or depositing, whether by single cell, battery, or other process. The requisites for preparing good depositing solutions, both for simple metals and alloys, with methods of making solutions generally, and of working them; suitable sources of electricity, including the dynamo-electric machine, voltaic batteries, together with their construction; as well as instructions for regulating the quantity and pressure of the current; regulating the quantity and quality of the deposited metal; cleaning and preparing metallic surfaces for receiving adhesive and non-adhesive deposits; copying works of art in various substances; elastic moulding; preparation of non-conducting surfaces to receive a deposit; multiplication of works of art by deposition; deposition by the various processes, of such metals and their alloys as antimony, bismuth, zinc, cadmium, tin, lead, iron, cobalt, nickel, copper, brass, german silver, mercury, silver, gold, platinum, and palladium; chemical relations of the cyanides of gold and silver; manufacture of cyanide of potassium; recovery of gold and silver from damaged solutions, &c.

THEORETICAL DIVISION OF THE SUBJECT.

1. **Facts.**—*One Metal in One Liquid.*—There are various modes in which deposition of one metal upon another may take place, and they may be classed as follows:—

Fig. 1.

1st. By the simple immersion of *one* metal in *one* liquid (Fig. 1), namely, by putting the metal to be coated into a solution of the metal to be deposited, and allowing it to remain a longer or shorter period of time, the liquid being at a suitable temperature; for instance, if we immerse a piece of clean iron in a solution of sulphate of copper, it will become coated with copper, but if we immerse a piece of silver in that liquid it will not become coated.

2nd. *Two Metals in One Liquid.*—By the immersion of *two* metals in *one* liquid (Fig. 2), the two metals being in contact with each other; for instance, if we connect a piece of silver A and a piece of iron B together, and immerse them in a solution of sulphate of copper C, the silver will become coated with copper as well as the iron; but if a piece of silver in contact with a piece of gold or platinum is immersed in the same liquid, it will not become coated. We have already seen that silver immersed alone in such a liquid will not receive a deposit of copper.

FIG. 2.

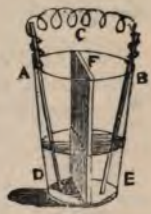

FIG. 3.

FIG. 4.

3rd. *One Metal in Two Liquids.*—By the immersion of *one* metal (*i.e.*, one *kind* of metal) in *two* liquids D and E (Figs. 3 and 4), the liquids being prevented from mixing with each other either by a porous partition F (Fig. 3) of bladder, thin wood, unglazed earthenware, or other porous material which will allow the two liquids to touch each other through its pores; the piece of metal being either bent so as to dip into each liquid, or cut into two portions, and its two ends united by a wire C, the end or piece to receive the deposit being immersed in one liquid, and the other piece in the other liquid (Fig. 3); or the two liquids being put in a deep narrow vessel, the heavier one being poured in first, and the lighter one poured carefully above it so as not to mix them together, and the piece of metal being in the form of a rod or wire placed vertically in the two liquids (Fig. 4.); for instance, if the lower liquid consists of a solution of sulphate of copper and the upper of dilute sulphuric acid, and a piece of copper is immersed in both liquids, that part of it which is in the sulphate solution will become coated with copper, whilst that in the acid liquid will be partly dissolved; but if, instead of copper, we use a piece of platinum, it will neither be dissolved nor receive a metallic deposit.

4th. *Two Metals in Two Liquids.*—By the immersion of *two* metals A and B (Fig. 5) in *two* liquids, D and E, the two being, as in the last arrangement, either separated by a porous diaphragm F, or poured one above the other, the two metals being immersed one in each liquid, and connected together by a wire C; for instance, if one

liquid is dilute sulphuric acid, and the other a solution of sulphate of copper, and a piece of copper is immersed in the dilute acid and a piece of silver in the metallic solution, the two metals being thus in mutual contact, the piece of copper will dissolve, and the silver receive a deposit of copper; but if we immerse a piece of platinum in the dilute acid with the silver in the sulphate solution, the platinum will not dissolve, nor the silver receive a metallic deposit.

FIG. 5.

FIG. 6.

5th. *Separate Depositing Liquid.*—By connecting any one of the foregoing arrangements, except the first, by means of wires with two separate pieces of metal of a similar kind immersed in a separate and suitable liquid (Fig. 6); for instance, if we take the arrangement of two metals in one liquid, such as iron B and copper C, in a solution of sulphate of copper A; or zinc B and silver C in dilute sulphuric acid A, and connect them by two separate wires D and E with two pieces of copper D and E immersed in a solution of sulphate of copper F contained in a separate vessel, the piece of copper E connected with the silver will dissolve, whilst the other piece D which is connected with the zinc will receive a deposit of copper; but if we substitute a solution of sulphate of zinc, freely acidulated with sulphuric acid, for the solution of sulphate of copper F, and two pieces of platinum for the pieces of copper, the one piece of platinum will not dissolve nor the other receive a metallic deposit.

6th. *Separate Depositing Liquid with any other Source of Power.*—By connecting the pieces of metal in the separate depositing liquid with any other source of depositing power, such as a dynamo, or a battery.

2. In these arrangements it will be observed that we have—1st, deposition by one metal and one liquid; 2nd, by two metals and one liquid; 3rd, by one metal and two liquids; 4th, by two metals and two liquids; 5th, by a separate depositing liquid and metals connected with either of these; and 6th, by a separate depositing liquid and metals connected with any other source of depositing power. These six classes and their combinations are capable of including all the known cases of electro-deposition.

FIG. 7.

3. Under the head of each of these classes will be mentioned a number of experiments with various metals and liquids; and it would be advisable for the student to try a few experiments, as he proceeds, both of deposition and non-

deposition of each class, in order to fix the facts more firmly in his memory, and give him a fuller comprehension of the principles.

4. **Depositing Arrangement, No. 1.**—Deposition by one metal and one liquid (Fig. 7) takes place in the following instances:—

Hydrochlorate of Terchloride of Antimony.—In a solution of hydrochlorate of terchloride of antimony (the ordinary chloride of antimony, as prepared for pharmaceutical purposes), bismuth, zinc, tin, lead, brass, and german silver become coated with antimony; whilst antimony, iron, nickel, copper, silver, gold, and platinum do not become coated.

Chloride of Bismuth.—In a solution of acid hydrochlorate of bismuth oxide (chloride of bismuth), zinc, tin, lead, and iron deposit the bismuth upon themselves, whilst antimony, bismuth, copper, brass, german silver, gold, and platinum do not.

Sulphate, Chloride, Nitrate, or Acetate of Zinc.—In a solution of either sulphate, chloride, nitrate, or acetate of zinc, neither antimony, bismuth, zinc, tin, lead, iron, nickel, copper, brass, german silver, silver, gold, or platinum become coated with zinc,

Protochloride of Tin.—In a solution of protochloride of tin, zinc and lead become tinned; whilst antimony, bismuth, tin, iron, nickel, copper, brass, german silver, silver, gold, and platinum receive no deposit.

Hyponitrate, Nitrate, or Acetate of Lead.—In a solution of hyponitrate, nitrate, or acetate of lead, zinc receives a coating of lead; whilst antimony, bismuth, tin, lead, iron, nickel, copper, brass, german silver, silver, gold, and platinum receive no deposit.

Ferrous Sulphate.—"Zinc," as Fischer says, "immersed in a perfectly neutral solution of ferrous sulphate (protosulphate of iron) contained in a stoppered bottle, throws down metallic iron, which is deposited partly on the zinc;" but in this solution neither antimony, bismuth, tin, lead, iron, nickel, copper, brass, german silver, silver, gold, or platinum receive any metallic deposit.

Sulphate of Copper.—In a solution of sulphate of copper, zinc, tin, lead, and iron become coated with copper; whilst antimony, bismuth, nickel, copper, silver, gold, and platinum do not.

Chloride of Copper.—In a solution of chloride of copper, bismuth, zinc, tin, lead, and iron receive a copper deposit; whilst antimony, nickel, copper, silver, gold, and platinum do not.

Nitrate of Copper.—In a solution of nitrate of copper, zinc, tin, lead, and iron become coated; whilst antimony, bismuth, nickel, copper, silver, gold, and platinum receive no deposit.

Dichloride of Copper.—With a solution of dichloride of copper in liquid ammonia, or of oxide of copper in a solution of sal-ammoniac, zinc receives a deposit; whilst antimony, bismuth, tin, lead, iron, nickel, copper, silver, gold, or platinum do not.

Mercurous Salts.—Solutions of mercurous salts have their metal deposited by arsenic, antimony, bismuth, zinc, cadmium, tin, lead, iron, copper, and brass, also by the alloys of silver with zinc, tin, lead, or copper.

Nitrate of Mercury.—A solution of nitrate of mercury yields its metal to bismuth, zinc, cadmium, lead, iron, or copper, and, if acidulated with nitric acid, to antimony also; but not to silver, gold, or platinum.

Acetate of Mercury.—Iron deposits mercury from a solution of acetate of mercury.

Silver Solutions.—The following metals, viz., manganese, arsenic, antimony, bismuth, zinc, cadmium, tin, lead, iron, copper, and mercury, deposit silver from its solutions in the metallic state; an aqueous solution of nitrate of silver yields its metal to manganese, arsenic, antimony, bismuth, zinc, tin, lead, iron, nickel, copper, brass, and german silver; but not to silver, gold, or platinum. Lead and tin deposit the silver most quickly; then follow the other metals in this order, cadmium, zinc, copper, bismuth, antimony, arsenic, mercury. Arsenic deposits silver from the alcoholic solution of nitrate of silver; antimony receives a coating of silver either in the aqueous sulphate or alcoholic nitrate; bismuth deposits silver from the alcoholic nitrate, but not from the aqueous sulphate; zinc receives a silver deposit in the alcoholic nitrate; tin becomes silvered in the alcoholic nitrate, but more quickly in the aqueous sulphate; iron deposits silver from the sulphate of silver; but not from alcoholic nitrate; copper deposits it from the aqueous sulphate of alcoholic nitrate; brass and the alloys of silver, with zinc, tin, or lead, deposit silver from silver solutions completely. In a solution of the double cyanide of silver and potassium (the ordinary plating liquid), zinc, lead, and copper become silvered; also brass and german silver, but more slowly; whilst antimony, bismuth, tin, iron, nickel, silver, gold, and platinum do not.

Gold Solutions.—From an acid solution of terchloride of gold, most of the base metals, likewise mercury, silver, platinum, and palladium deposit gold, generally in the metallic state, but not always; arsenic rapidly deposits gold in this solution; antimony, tellurium, and bismuth become gilded; zinc, cadmium, lead, iron, cobalt mercury, silver, platinum, and palladium deposit the gold. In a solution of the double cyanide of gold and potassium, zinc quickly becomes gilded, and copper, brass, and german silver slowly; whilst antimony, bismuth, tin, lead, iron, nickel, silver, gold, and platinum do not.

Bichloride of Platinum.—Platinum is deposited from a solution of its bichloride by arsenic, antimony, tellurium, bismuth, zinc, cadmium, tin, lead, iron, cobalt, nickel, copper, brass, german silver, mercury, and silver; but not by gold or platinum.

5. *Observations upon Class of Instances, No. 1.*—In reviewing all these instances, we may make the following observations :—1st, that various metals by mere immersion in solutions of other metals, at the ordinary temperature of the atmosphere, sometimes become coated with a deposit of metal, and sometimes not; 2nd, that no metal becomes coated by mere immersion in a solution of the same metal—for instance, zinc does not become coated with zinc in a solution of sulphate of zinc; copper with copper in a solution of its sulphate, gold with gold in its chloride; 3rd, that the baser metals, especially zinc, cadmium, tin, lead, and iron, become coated more frequently than the noble metals, especially gold and platinum; 4th, that solutions of base metals, especially of zinc and iron, yield their metal less frequently than those of the noble metals, especially those of gold and platinum; 5th, that of all the ordinary metals mentioned in the foregoing instances, zinc deposits metal from the greatest number of solutions, and appears to have the strongest depositing power; 6th, that the coherent and adhesive deposits obtained are in all cases exceedingly thin; and 7th, that oftentimes the deposited metal, whatever its kind may be, has the appearance of a black or dark-coloured powder on its surface, especially when it has been deposited, very rapidly; and that sometimes it exhibits its ordinary colour and appearance, especially if its outer portion is rubbed off.

6. To this mode of depositing belongs the process of tinning brass articles (wash tinning), by boiling them in water containing a salt of tin and bitartrate of potash; the process of silvering brass nails, buttons, hooks and eyes, buckles, &c., by rubbing them with any of the well-known silvering compositions moistened with water; also the water gilding process, &c.

7. **Depositing Arrangement, No. 2.**—*Deposition by Two Metals and One Liquid.*—The following instances belong to the class of deposition by two metals and one liquid, the two metals being either in mutual contact (touching each other either above or beneath the liquid), or connected by a wire.

FIG. 8.

Chloride of Antimony.—For instance, if we immerse a piece of antimony A, in contact with a piece of zinc B, in a solution of the ordinary chloride of antimony C, it will receive a coating of antimony; or if we immerse a piece of platinum in contact with a piece of tin in this liquid, it will receive a deposit of antimony; but if we immerse a piece of antimony in contact with a piece of platinum, or a piece of platinum in contact with a piece of silver in this liquid, it will receive no metallic deposit.

Chloride of Bismuth.—In a solution of chloride of bismuth, brass in contact with a piece of zinc, copper in contact with tin, or germau

silver with iron, receives a deposit of bismuth; but brass in contact with a piece of gold, gold in contact with silver, or german silver with platinum, receives no deposit.

Sulphate, Chloride, or Nitrate of Zinc.—With a solution of either sulphate, chloride, or nitrate of zinc, no metal of any pair of metals selected from amongst the following will receive a deposit of zinc: antimony, bismuth, zinc, tin, lead, iron, nickel, copper, mercury, silver, gold, platinum, or palladium.

Protochloride of Tin.—With a solution of protochloride of tin, either antimony, tin, or copper immersed in contact with zinc or lead, will receive a coating of tin; but antimony in contact with tin, tin with silver, copper with iron, or either gold or platinum with copper will not receive a deposit.

Hyponitrite of Lead.—With a solution of hyponitrite of lead, either tin, copper, or brass, in contact with a piece of zinc, will receive a deposit of lead; but tin in contact with copper, copper with lead, or brass with platinum, receives no deposit.

Nitrate of Lead.—With a solution of nitrate of lead, either copper, brass, or silver, in contact with zinc, receives a coating of lead; but copper in contact with iron, brass with tin, or silver with copper, receive no such coating.

Protosulphate of Iron.—With a saturated solution of protosulphate of iron, platinum in contact with zinc receives a deposit of iron; but in contact with copper it receives no metallic deposit.

Chloride of Nickel and Ammonia.—In a solution of the double chloride of nickel and ammonia, copper in contact with zinc receives a deposit of nickel; but in contact with silver it does not receive such a deposit.

Sulphate of Copper.—In a solution of sulphate of copper, brass in contact with zinc; or tin, german silver, silver, or platinum, in contact with iron, receives a deposit of copper; whilst silver in contact with antimony, or platinum in contact with brass, receives no deposit.

Oxide of Copper in Ammonia.—In a solution of oxide of copper in ammonia, platinum in contact with zinc receives a deposit; but silver in contact with iron does not.

Nitrate of Mercury.—In a solution of nitrate of mercury, silver in contact with either zinc or iron, or platinum in contact with copper, receives a metallic deposit; platinum in contact with silver does not.

Nitrate of Silver.—In a solution of nitrate of silver, gold in contact with zinc receives a deposit of silver; but in contact with platinum it does not.

Bichloride of Platinum.—In a solution of bichloride of platinum, platinum in contact with zinc becomes coated with platinum; but in contact with gold it receives no such coating.

8. *Observations upon Class of Instances No.* 2.—The following general observations may be made upon the foregoing facts :—1st, that in some instances deposition does, and in others it does not, occur; 2nd, that no metal will cause another metal to be coated by this method, unless it can coat itself in the same liquid by simple immersion. Raoult has observed that a piece of gold in contact with a piece of cadmium in a concentrated and boiling hot solution of chloride of cadmium, acquires a thin film of deposited cadmium; in this case a metal deposits itself. For instance, zinc cannot usually coat itself in solutions of zinc, neither can it cause other metals to become coated with that metal in those solutions; copper cannot coat itself with zinc in a solution of sulphate of zinc, or with tin in a solution of chloride of tin, neither can it cause silver, gold, or any other metal, to become coated with zinc or tin, in those liquids; 3rd, that one of the two metals which receive a deposit by this method, derives its power of receiving the deposit by virtue of its contact with the other metal; 4th, that any metal which has the power of coating itself by simple immersion in a given liquid, can by this method cause other metals which do not coat themselves by simple immersion in that liquid to become coated—for instance, zinc, tin, and iron coat themselves with copper by simple immersion in a solution of sulphate of copper, and silver, gold, and platinum do not; but if either of the former metals be connected with either of the latter, and the two immersed together in that liquid, the latter metals as well as the former will become coated with copper; 5th, that base metals, and especially zinc, have generally the power of causing other metals to become coated by this method; whilst the noble metals, and especially gold and platinum, rarely possess this power; 6th, that by this method metal is deposited much more frequently from solutions of the noble metals than from those of the base ones; and 7th, that thick deposits of metal may be obtained by this method, provided the action is continued sufficiently long, and the liquid is properly renewed.

FIG. 9.

FIG. 10.

9. **Depositing Arrangement No. 3.**—*Deposition by One Metal and Two Liquids—Chloride of Antimony.*—The following instances belong to deposition by the immersion of one metal in two liquids, D and E

(Fig. 9), separated by a porous diaphragm F, the metal being either in two pieces connected together by a wire or wires C, or in one piece, and bent so as to dip into both liquids; the diaphragm may be dispensed with, as already explained, by pouring the lighter liquid carefully above the other, and placing the piece of metal vertically in the two liquids; if two pieces of antimony, A and B, connected together by a wire or wires C, are immersed, one in dilute nitric acid D, and the other in a solution of chloride of antimony E, the piece in the dilute acid will dissolve, whilst that in the chloride solution will receive a metallic deposit.

Chloride of Bismuth.—If two pieces of antimony are immersed in the previous manner, one in hydrochloric acid, and the other in a solution of chloride of bismuth, that in the acid will dissolve, and the other receive a coating of bismuth.

Sulphate of Copper.—With antimony, in dilute hydrochloric acid on one side, and in a solution of sulphate of copper on the other, a deposit of copper is obtained.

Chloride of Bismuth.—With bismuth in hydrochloric acid on one side, and in a solution of chloride of bismuth on the other, a free deposit of bismuth is soon obtained.

Chloride of Zinc.—If a piece of zinc is bent so as to dip into dilute hydrochloric acid on one side, and into a neutral solution of chloride of zinc on the other, a free deposit of zinc will be found upon the end in the metallic solution after a period of twelve hours.

Solution of Acetate of Zinc.—With zinc in a solution of acetate of zinc on one side, and in dilute sulphuric acid on the other, that in the dilute acid will dissolve, whilst the other end will receive a metallic deposit.

Iron in Chloride of Antimony.—With iron in dilute sulphuric acid on one side, and in a solution of chloride of antimony on the other, the end in the metallic solution will receive a deposit of antimony, whilst that in the dilute acid will dissolve.

Iron in Sulphate of Zinc.—With iron in dilute sulphuric acid on one side, and in a solution of sulphate of zinc on the other, no deposit of zinc is obtained in twelve hours; similarly with iron, dilute sulphuric acid, and a solution of protosulphate of iron, no deposit occurs in twelve hours.

Tin in Chloride of Tin.—With tin in dilute hydrochloric acid on one side, and in a solution of chloride of tin on the other, a deposit of tin is obtained.

Zinc in Sulphate of Zinc.—With zinc in dilute sulphuric acid, and in a solution of sulphate of zinc, a free deposit of zinc occurs in twelve hours.

Bismuth in Nitrate of Bismuth.—With bismuth in dilute nitric acid, and in a solution of acid nitrate of bismuth, a thin deposit of bismuth is found in twelve hours.

Copper in Sulphate of Zinc.—With copper in dilute sulphuric or dilute nitric acid on one side, and in a solution of sulphate of zinc on the other, no deposit of zinc occurs in twelve hours.

Brass or Copper in Sulphate of Copper.—With brass or copper in dilute sulphuric acid on one side, and in a solution of sulphate of copper on the other, a deposit of copper is obtained in twelve hours; similarly with copper in dilute hydrochloric acid, and in a solution of chloride of copper, a metallic deposit occurs.

Silver in Plating Liquid.—With silver in either dilute sulphuric, or dilute nitric acid on one side, and in a solution of sulphate of copper on the other, no deposit of copper takes place in twelve hours; but with silver in a solution of cyanide of potassium on one side, and in the double cyanide of potassium and silver on the other, a free deposit of silver takes place upon the end or piece in the latter solution.

Platinum in Nitrate of Copper.—With platinum in aqua regia on one side, and in either a solution of nitrate of copper, the ordinary cyanide gilding solution, or a solution of bichloride of platinum on the other, no deposit of copper, gold, or platinum occurs.

10. *Observations on Class of Instances No.* 3.—1st, it appears, that in this class also we obtain negative as well as positive instances; 2nd, that by this arrangement, unlike the previous classes, almost any metal may cause the same metal to be deposited—for instance, zinc may deposit zinc, copper deposit copper, and silver deposit silver; 3rd, that by it even a noble metal may cause the deposition of a base metal, provided we have a suitable combination of liquids; for instance, if a piece of gold or silver is immersed in a strong solution of cyanide of potassium on one side, and in a solution of sulphate of copper or chloride of antimony on the other, the end in the free cyanide solution will dissolve, whilst that in the copper or antimony liquid will receive a deposit; 4th, that the metal or end which receives a deposit derives that power from its contact with the metal in the other liquid; 5th, that, as a general rule, base metals have a greater power of causing deposition by this method than the noble ones; 6th, that the noble metals are more readily and more often deposited than the base ones; and 7th, that we may produce thick and coherent deposits by this method.

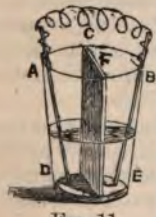

FIG. 11.

11. **Depositing Arrangement No. 4.**—*Deposition by Two Metals and Two Liquids.*—The following instances belong to the class of deposition produced by the immersion of two metals, A and B (Fig. 11), in two liquids, D and E, the metals being in mutual contact or connected together by a wire C, and the liquids separated by a porous partition F.

Zinc Depositing Antimony.—If a piece of antimony A be immersed in a solution of chloride of antimony D, and a piece of zinc B is immersed in dilute sulphuric acid E, and the two metals are connected together by a wire or wires C, a free deposit of antimony upon the metal A will take place in twelve hours.

Tin Depositing Zinc.—With tin and hydrochloric acid, and zinc in a neutral solution of sulphate of zinc, a deposit of zinc is obtained in the metallic solution.

Iron Depositing Antimony.—With iron in dilute hydrochloric acid, and antimony in chloride of antimony, a copious deposit of antimony takes place in twelve hours.

Magnesium Depositing Zinc.—With magnesium in dilute sulphuric acid, and zinc in a solution of sulphate of zinc, a deposit of zinc occurs.

Zinc Depositing Copper.—With zinc in dilute sulphuric acid, and brass in a solution of sulphate of copper, copper is deposited.

Bismuth Chloride of Antimony.—With bismuth in dilute hydrochloric acid, and antimony in chloride of antimony, no deposit of the latter takes place in twenty-four hours.

Iron and Chloride of Tin.—With iron in dilute hydrochloric acid, and tin in a solution of chloride of tin, no deposit of tin occurs in eighteen hours.

Copper and Chloride of Antimony.—With copper in dilute hydrochloric acid, and antimony in chloride of antimony, or tin in chloride of tin, no deposit of antimony or tin took place in twenty hours.

12. *Observations upon Class of Instances No.* 4.—1st, It appears that negative as well as positive instances occur in this arrangement in common with the others; 2nd, that by using suitable metals and liquids, deposition may be effected more rapidly by this method than by the preceding ones; 3rd, that the metal which receives the deposit derives its power from its contact with the other metal; 4th, that base metals in strong acids have the greatest power of causing a deposit upon the other metals, and noble metals the least; 5th, that the noble metals are more readily deposited than the base ones; and 6th, that thick and coherent deposits may be obtained.

In all the above instances, instead of using one vessel divided into two parts by a porous diaphragm, it will be found convenient to put one of the liquids in an unglazed earthenware porous cell, and immerse the cell in the other liquid (see vessel A, Fig. 13). In this case, either liquid may be the outer vessel. This last arrangement (No. 4) is usually termed the "single cell" process.

13. **Depositing Arrangement No. 5.**—*Deposition by Separate Liquid.*—The next class of instances are those in which either of the foregoing

arrangements, except the first, is connected by wires with two pieces of similar metal immersed in a separate liquid. For instance:—

1st. *With Two Metals and One Liquid* (Fig. 12).—If we take a vessel A containing either dilute sulphuric acid or a solution of sulphate of copper, and immerse in it a piece of zinc B and copper C, with copper wires D and E attached to them, and either immerse the free ends of those wires in a separate solution of sulphate of copper F, or connect them with two pieces of copper immersed in that liquid, the piece of copper E in liquid F will dissolve, whilst the opposite piece D, connected with the zinc, will receive a deposit of copper.

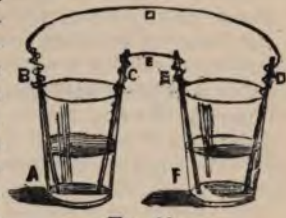

Fig. 12.

2nd. *With One Metal and Two Liquids.*—If we take a vessel A (Fig. 13) containing a porous cell B, with a neutral solution of sulphate of zinc C in the outer vessel, and dilute sulphuric acid D in the inner, and immerse two pieces of zinc E and F, with copper wires G and H attached, into D and C respectively, and immerse the ends of those wires in a separate solution of sulphate of copper I, the end of the wire H will dissolve, whilst that of G will receive a deposit of metallic copper.

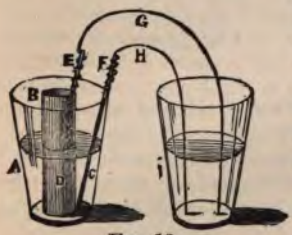

Fig. 13.

3rd. *With Two Metals and Two Liquids* ("separate cell" arrangement, Fig. 13). If we substitute a piece of copper for the piece of zinc F in the last-mentioned instance, and a solution of sulphate of copper for that of sulphate of zinc, similar effects will take place at the ends of the wires in the liquid I, except that the action will be much more rapid; but if in either of these three instances we use a solution of sulphate of zinc freely acidulated with sulphuric acid, instead of the solution of sulphate of copper I, and platinum wires in place of the copper ones to be immersed, neither of the pieces of platinum will dissolve or receive a metallic deposit.

14. *Remarks upon Class of Instances No. 5.*—In this class of instances the method or arrangement differs from the three preceding ones, simply by the wires which connect the two pieces of metal being cut in two, and its free ends either immersed in a separate liquid or connected with two pieces of metal dipping into that liquid. It is not necessary to have the depositing vessel perfectly separated; it may even be attached to

the same piece of apparatus, provided the liquid in it is perfectly separated from the other liquids and metals. The pieces of metal in the separate liquid possess no power of deposition of themselves in that liquid, even if they were connected together, but derive their power of dissolving and receiving a deposit wholly from the other metals and liquids by means of the wires.

15. **Depositing Arrangement No. 6.**—*Deposition by Magnet and Coil* (Fig. 14).—We may produce deposition in the separate liquid by connecting the two pieces of immersed metal with any other source of depositing power—for instance, if a long copper wire, covered with silk or cotton, is coiled upon a large bar of pure soft iron B, and its ends C and D are immersed in a solution of sulphate of copper E, and the poles of a powerful horse-shoe magnet F are brought in contact very many times with the ends of the bar, and every time before removing the magnet from the bar, one of the ends of the wire is taken out of the liquid, and replaced before returning the magnet, one end of the copper will slightly dissolve, and the other receive a thin copper deposit; but if each of the ends is allowed to remain constantly in the liquid, no such effects will occur; because the removal of the magnet produces an opposite current, which undoes the effects.

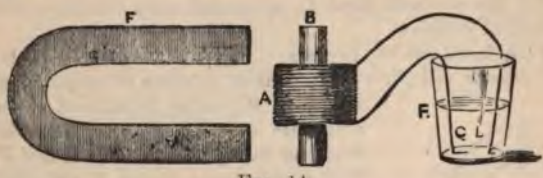

FIG. 14.

16. **Compound Depositing Arrangement No. 7.**—Any of the foregoing combinations of liquids and metals (except the first), or the

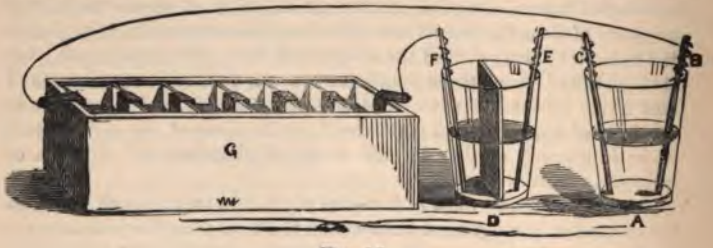

FIG 15.

magnetic arrangement, with or without separate depositing liquids, may be connected together in a *series* of any number, and may include

each of the arrangements in the same series, or include any number of depositing liquids, and deposition may be obtained either in the whole or in any portion of them at the same time; for instance, the vessel A (Fig. 15) contains a piece of zinc B, and copper C, immersed in dilute sulphuric acid; vessel D contains zinc E, in dilute sulphuric acid, and copper F, in a solution of sulphate of copper; vessel G contains a series of separate depositing liquids, consisting of solution of sulphate of copper, connected together by bent pieces of copper; the extreme pieces being attached to zinc B and copper F; here deposition takes place upon every alternate piece of copper throughout the whole series, except that in vessel A. In vessel A hydrogen instead of copper is deposited.

17. **General Observations.**—We may make the following general observations upon the whole of the foregoing facts:—1st, that negative as well as positive instances occur in all classes of facts of electro-deposition; 2nd, that almost any of the ordinary metals, both noble and base, may be deposited by each of the methods or arrangements described; 3rd, that the particular result of deposition or non-deposition occurring, appears to depend chiefly upon the particular combination of liquids and metals, their arrangement and connections; 4th, that the size or shape of the containing vessels, the bulk or depths of the liquids, the size, form, or position of the metals, appear to exercise little or no influence upon the result; 5th, that in all cases of deposition there is a difference in *kind*, either of the metal, of the liquid, or of both; 6th, that in all such cases a metal dissolves in a liquid; for instance, in Arrangement No. 1, with a piece of iron immersed in a solution of sulphate of copper, a portion of the iron is dissolved as the copper is deposited; in Arrangement No. 2, with iron and copper together in a solution of sulphate of copper, the iron dissolves and the copper receives a deposit: in Arrangement No. 3, with copper in dilute sulphuric acid, and in a solution of sulphate of copper, the copper in the acid dissolves, whilst that in the metallic solution receives a deposit; in Arrangement No. 4, with zinc in dilute sulphuric acid, and copper in sulphate of copper, the former dissolves, whilst the latter receives a deposit; in Arrangements Nos. 5 and 6, one piece of metal in the separate depositing liquid dissolves, whilst the other receives a metallic deposit, and the same with the Compound Arrangement No. 7; 7th, that in Arrangements Nos. 1 and 2, the same piece of metal which dissolves also receives a metallic deposit, and in Arrangements 3, 4, 5, 6, and 7, the pieces of metal which receive a deposit do not dissolve; 8th, that as a general rule in all methods, and in all solutions except alkaline metallic cyanides, zinc among common metals has the greatest, and platinum the least power of producing deposition: 9th, that zinc generally deposits metals most rapidly from

their solutions, and most frequently in the state of a dark-coloured or black powder; and 10th, that among solutions of the salts of ordinary metals, those of the salts of noble metals yield their metal most easily, and those of the base metals, zinc especially, with the greatest difficulty.

18. In looking over the foregoing instances, we also observe:—1st, that when several metals are used, they must either *touch* each other or be connected together by wires or other pieces of *metal;* 2nd, that when several liquids are used, they also must *touch* each other, either by means of a porous diaphragm, or otherwise; 3rd, that when a series of metals and liquids are used, they must together form a *complete circuit*, and all their points of contact be perfectly clean; 4th, that a separate depositing liquid possesses no power of deposition by itself, but derives its power by means of the wires from the other arrangements with which it is connected; and 5th, that the length of the connecting wire has no very great influence on the result. These observations have led us to conclude that deposition is caused by some *force* which is generated in some part of the apparatus, and circulates through the liquids, metals, and wires which compose the circuit.

19. Principles.—*Conditions of Electro-Deposition.*—From the simple *facts* of electro-deposition, and the general observations made upon them, we proceed to consider the *causes* of deposition, and the conditions or circumstances under which deposition occurs, in the following order:—

1st. *The Chemical Conditions.*—If we immerse a clean iron wire in a solution of nitrate of mercury, it receives a deposit of that metal; but if we immerse it in perfectly dry metallic mercury, it receives no deposit, because in the former case the necessary chemical conditions of deposition are present, whilst in the latter case they are absent.

2nd. *The Electrical Conditions.*—If we connect together a piece of iron and a piece of copper by means of a metal wire, and immerse them in a solution of sulphate of copper, the copper will receive a metallic deposit; but if we connect them together by a cord of gutta-percha or rod of glass, no deposit will take place, because in the former case all the electrical conditions are present, whilst in the latter case one of them, viz., a complete conducting circuit, is absent.

3rd. *The Thermic Conditions* remain imperfectly investigated.

4th. *The Mechanical Conditions.*—If a piece of iron be immersed in a solution of sulphate of copper, it receives a copper deposit; but if a piece of platinum be so immersed it receives no such deposit, because, for one reason, in the former instance the mechanical conditions of attraction and repulsion at the dissolving and depositing surfaces are present, but in the latter they are absent.

5th. *The Mathematical Conditions.*—If we immerse two pieces of carbon in fused *proto*-chloride of tin, and connect them with a voltaic battery, tin will be deposited; but if we immerse them in *bi*-chloride of tin no deposition will occur, because in the first instance all the mathematical conditions are present; the fluid salt contains *one* atom of chlorine for each atom of tin; whilst in the latter case one of them is absent, the salt contains *two* atoms of chlorine to one atom of tin, and, according to Faraday's law, "only those substances of the first order are directly decomposible which contain one atom of one of their elements for each atom of the other."

These several heads are capable of including all the known circumstances or conditions under which deposition occurs; and under the head of each of them will be given a few instances, both of deposition and of non-deposition, to illustrate the principle; and it would be advisable for the reader to try for himself some of the experiments given, in order to fix the principles more firmly in his memory.

20. Chemical Conditions of Deposition.—The first chemical condition to be observed is, that in every case of deposition the depositing liquid contains acid and basic elements, namely, a salt, the acid of which is to dissolve or combine with one metal, and its metal or base to be deposited upon the other.

1st. *Deposition by One Metal and One Liquid.*—With the first class of facts, if we immerse a piece of clean iron in a solution of nitrate of mercury, it will receive a deposit of that metal; but if we immerse it in mercury alone, it will receive no deposit; in the first instance an acid as well as a basic substance was present, and deposition took place; but in the second instance the metal or base alone was present, and no deposition occurred.

2nd. *With Two Metals and One Liquid.*—If zinc and platinum are immersed in mutual contact in a solution of nitrate of mercury, the platinum will receive a metallic deposit, but if they are immersed in pure dry mercury, no deposit will occur.

3rd. *With One Metal and Two Liquids.*—If we immerse one end of a platinum wire in a strong solution of cyanide of potassium, and its other end in a solution of nitrate of mercury, the two liquids being in mutual contact by means of a porous partition, the end in the metallic solution will soon receive a deposit of mercury; but if perfectly dry mercury is substituted for the nitrate solution, no such deposit will occur.

4th. *With Two Metals and Two Liquids.*—If we immerse zinc in dilute sulphuric acid, and platinum in a solution of nitrate of mercury, the two liquids touching each other by a porous partition, and the metals connected together by a wire, the platinum will quickly

receive a deposit of mercury; but with dry mercury instead of the metallic solution, the platinum will not receive a deposit.

5th. *With a Separate Depositing Liquid.*—If we take two pieces of platinum wire, connect them, as already described (13), with either of the foregoing Arrangements, or with a magnet and coil (15), and immerse their free ends in a solution of nitrate of mercury, one of the wires will receive a deposit of mercury; but if the separate liquid consist only of dry mercury, no deposit will be obtained.

It is evident from these facts, that in every case where deposition occurs, the depositing liquid contains both acid and basic substances, and that without the presence of both no deposition takes place.

21. **Degrees of Chemical Affinity of Metals and Liquids.**—At the present point it is necessary to mention a few instances of the different degrees of chemical affinity manifested by different metals and liquids, that the reader may be able to understand their general chemical relations in electro-deposition more clearly:—

1st. If we immerse a piece of potassium in almost any liquid, very violent chemical action takes place, which is stronger in mineral and vegetable acids than in water or organic liquids; if we place a small piece of it upon water, violent chemical action occurs, the water is decomposed, heat is produced, gas is evolved and takes fire, the metal melts and rolls about on the surface of the water, oxidates and dissolves.

2nd. If we immerse a piece of zinc in any of the strong mineral acids (sulphuric, hydrochloric, hydrofluoric, or nitric acids), strong chemical action takes place, gas is freely evolved, and the metal oxidates and dissolves; with solutions of the ordinary vegetable acids, *i.e.*, oxalic, tartaric, citric, formic, and acetic acids, the same effects occur in a much weaker degree; but with water there is no visible decomposition, no gas evolved, nor any perceptible chemical action; these instances show that potassium has a much stronger affinity for liquids than zinc, and that both the negative elements of these metals have a stronger affinity for acids than for water.

3rd. If we immerse a piece of zinc successively in each of the ordinary mineral and vegetable acids diluted with water, it will be quickly dissolved, with evolution of hydrogen gas in nearly all of them; but if we immerse a piece of copper in those liquids, it will be quickly dissolved in only one of them, viz., nitric acid, and from this we conclude that copper has generally a much weaker affinity for acids than zinc.

4th. If we immerse either gold or platinum in any of the strong mineral or vegetable acids, or even in cold aqua regia, it will be nearly unaffected in all of them, whilst copper would be rapidly acted upon by nitric acid or by aqua regia, and slowly by several of the others,

thereby showing that the affinity of gold or platinum for acids is generally much weaker than that of copper.

From the foregoing, and many other instances that might be mentioned, we conclude that the degree of affinity of the metals for acids is usually in the following order, namely, potassium, zinc, copper, gold, platinum. Hydrocyanic acid and cyanogen appear to differ in one respect, in their chemical relations towards ordinary metals, from oxygen, chlorine, and the ordinary mineral and vegetable acids, in having a much stronger affinity for noble metals, and weaker for the base metals; this is probably one of the chief reasons for the extensive adoption of cyanogen compounds in electro-deposition; those compounds are highly suitable for the deposition of noble metals, because of the great affinity of cyanogen for those metals, but not, as some persons assert, for the deposition of many of the base metals, on account of its comparatively weak affinity for them. Upon iron it has but little action.

22. Potassium is an *alkali* metal; zinc, cadmium, tin, lead, iron, cobalt, nickel, and copper are *base* metals; and mercury, silver, gold, platinum, palladium, &c., are *noble* metals; and of these three classes, the alkali metals possess the strongest affinity for acids, base metals intermediate, and noble metals the least. The same order prevails in their degrees of depositing power; potassium and the alkali metals generally deposit nearly all metals from their solutions; zinc, and the base metals generally, deposit a smaller number; and gold, platinum, and the other noble metals deposit very few from their solutions; thus we perceive that those metals which have the strongest chemical affinity for acids, possess the greatest depositing power, and those which have the least affinity for acids, have also the least depositing power.

23. **Difference of Chemical Affinity Necessary to Deposition.**—The second chemical condition which we have to observe is, that in every case of *deposition* there is a *difference* of chemical affinity at the dissolving and receiving surfaces for the different elements of the liquid, and that the dissolving metal has a stronger affinity for the acid elements of the liquid than either the metal in solution or the receiving metal; for instance:—

1st. *With One Metal and One Liquid.*—If we immerse a piece of iron in a solution of sulphate of copper, a deposit takes place upon it, but if we immerse a piece of platinum in the liquid, it receives no deposit; in the first case, the iron having a stronger affinity for the sulphuric acid of the salt than copper, combines with it and dissolves, and the copper thereby set free from the acid is deposited upon the iron; whilst in the second case, platinum having a much weaker

affinity for the acid than the copper, cannot take the acid from the copper, and therefore cannot cause deposition.

2nd. *With Two Metals and One Liquid.*—If we immerse copper and iron in mutual contact, in a solution of sulphate of copper, the iron dissolves, and deposition of copper takes place upon both metals; but if we immerse copper and platinum in mutual contact in this solution, no deposition occurs. In the first instance, the iron possessing a stronger chemical affinity for sulphuric acid than the copper, combines with it, and sets the copper free; by this action, a current of depositing force is generated, which circulates through the iron, liquid, and copper, at their points of contact, and causes the metal of the liquid to be deposited upon the piece of copper; but in the second case, neither the copper nor platinum possessing a stronger affinity for the acid of the salt than its associated metal, there is no copper set free, no sufficiently strong current of depositing force generated, and consequently no deposition takes place.

3rd. *With One Metal and Two Liquids.*—If we immerse one end of a piece of copper in dilute sulphuric acid, and the other in a solution of sulphate of copper, the two liquids touching each other, copper will be deposited upon the end immersed in the metallic solution, whilst the other end will combine with the acid and dissolve; but if a piece of platinum or gold is substituted for the copper, neither of its ends will dissolve or receive a metallic deposit; in the first instance, the dilute sulphuric acid, having a stronger affinity for copper than a solution of sulphate of copper, combines with it, causes it to dissolve, develops a current of depositing force which circulates through the metals and liquids, and a deposit of copper is produced; whilst in the second instance, the platinum or gold having a weaker affinity for the acid of one liquid than copper for the acid of the other liquid, cannot separate the copper, or cause deposition.

4th. *With Two Metals and Two Liquids.*—If we immerse a piece of silver in a strong solution of cyanide of potassium, and a piece of copper in a solution of the double cyanide of copper and potassium, the liquids touching each other by a porous partition, and the metals mutually touching by a wire, the silver will dissolve, and the copper receive a metallic deposit; but if a piece of iron is substituted for the silver, no deposit will occur. In the first instance, the one solution has a stronger affinity for the silver than the other has for the copper, consequently the former is dissolved, a current or depositing force is generated, and copper deposited; but in the second case, the one liquid has a weaker affinity for iron than the other has for copper, and therefore no iron is dissolved, no depositing force *generated*, and no copper deposited.

5th. *With a Separate Depositing Liquid connected with any Source of Depositing Power.*—If we connect two pieces of silver with any of those sources of power, and immerse them in a solution of cyanide of potassium, one piece will quickly dissolve, and the other after a while receive a deposit of silver; but if pieces of iron are first used instead of silver, neither will dissolve or receive a metallic deposit.

In every case where a separate depositing liquid is used, the two pieces of metal immersed in it have a *difference* of chemical affinity imparted to them by means of their connection with some arrangement which develops depositing force, and this difference of affinity is manifested most when the liquid has a strong affinity for the immersed metal, and least when it has a weak affinity for that metal; so in the first of the two immediately preceding instances, the liquid having a strong affinity for silver, allows this difference of affinity to be freely exercised at the immersed surfaces of the two pieces of metal, and consequently one dissolves, and the other receives a deposit; but in the second of these instances, the liquid having a very weak affinity for iron, does not admit of the exercise of this difference of affinity, and hence neither piece dissolves or receives a deposit. From these instances it is manifest that whenever deposition occurs, there is a difference of chemical affinity between the dissolving and receiving surfaces for the different elements of the liquid; that the dissolving metal has a stronger affinity for the acid elements than the receiving one; and that without this condition no deposition occurs.

24. It must be mentioned also that the metals which have the greatest difference in their degrees of affinity for acids, are those which evolve the greatest strength of depositing power, for instance:—

1st. *With One Metal and One Liquid.*—If we immerse a piece of silver in a solution of terchloride of gold, it slowly becomes gilded, but if we immerse a piece of zinc in it, gold is almost instantaneously deposited; because, in the former case, the difference of affinity between gold and the immersed metal for the acid of the liquid is very much smaller than in the latter case.

2nd. *With Two Metals and One Liquid.*—If we immerse a piece of platinum and a piece of copper, in mutual contact, in a solution of nitrate of silver, the platinum will become silvered, but much more slowly than if iron or zinc were used in place of the copper, because there is a greater difference of affinity between platinum and iron or zinc for the acid of the liquid, than between platinum and copper; or, if we immerse a piece of zinc and a piece of platinum or platinized silver in dilute sulphuric acid, and connect them separately with two pieces of copper immersed in a separate solution of sulphate of copper, copper will be dissolved and deposited in the separate liquid more

rapidly than if we used zinc and copper in place of zinc and platinum, and much more rapidly than if we used iron and copper; because the difference of affinity between zinc, platinum, or platinized silver for dilute sulphuric acid, is more than zinc and copper for that liquid, and much more than between iron and copper.

3rd. *With Two Metals and Two Liquids*—If we immerse a piece of zinc in dilute sulphuric acid, and a piece of copper in a solution of sulphate of copper, the two liquids touching each other, and the two metals connected with two pieces of copper in a separate solution of sulphate of copper, the amount of metal dissolved and deposited in a given time in the separate liquid will be much smaller than if we used zinc in dilute sulphuric acid, and platinum in strong nitric acid; because the difference of affinity between the two metals in the two liquids, in the first instance, is less than in the second.

25. **Acid and Basic Affinities Necessary.**—Chemical affinity differs not only in degree but also in kind; basic substances, such as metals, alkalies, alkaloids, and most metallic oxides, have a great tendency to combine with acids; whilst acid substances, such as the metalloids (oxygen, sulphur, chlorine, phosphorus, fluorine, &c.), mineral and vegetable acids, and some metallic oxides, tend to combine with bases. In a similar manner, the difference of affinity between the dissolving and receiving surfaces in electro-deposition is not wholly one of degree, but is also one of kind; the dissolving metal in a separate depositing liquid (13) acquires, by means of its connexion with some source of depositing power, an affinity for the *acid* elements of the liquid; whilst the receiving metal acquires, by the same means, an affinity of an opposite kind; for instance (Fig. 16), if a piece of platinum A and a piece of zinc B are immersed in dilute sulphuric acid C, some mercury D placed at the bottom of a separate solution of protosulphate of iron E, a piece of iron F immersed in this liquid and connected by a wire with the platinum, and the mercury connected by an iron or platinum wire G, which is prevented from touching the liquid by a tube of glass or gutta-percha, the immersed piece of iron will exercise one kind of affinity, combine with the acid of the dissolved salt, and form a definite chemical compound (protosulphate of iron), containing one equivalent of iron and one equivalent of sulphuric acid; whilst the mercury will exercise an opposite kind of affinity, and combine with the metal or base of the salt, forming likewise a definite chemical compound (FeHg), containing one equiva-

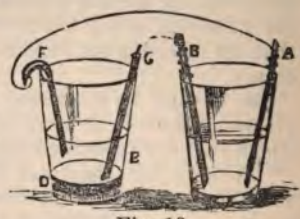

Fig. 16.

lent of iron and one of mercury. If a solution of sulphate of copper is substituted for that of sulphate of iron, and a piece of copper for the piece of iron, a similar definite compound of copper and sulphuric acid is formed at the dissolving plate, and of copper and mercury (CuHg) at the receiving metal.

These experiments prove in a most satisfactory manner that, in the act of deposition, the surface of the dissolving metal possesses one kind of affinity by virtue of which it tends to attract *acid* substances, and combine with them in definite proportions; and the surface of the receiving metal possesses an opposite kind of affinity, by virtue of which it tends to attract and combine with *basic* substances, also in definite proportions. Mercury is the only metal which has been observed to manifest this definite affinity at the receiving surface, probably because it is the only metal fluid at ordinary temperatures, fluidity being an essential condition of such affinity; but it is likely that other metals would also manifest this tendency, if kept in a melted state in contact with suitable fused salts, and properly acted upon by depositing force.

26. **Fluidity Essential to Electro-Deposition.**—The affinities of electro-deposition, like those of ordinary chemical action, require, generally speaking, one at least of the combining bodies to be in the liquid state; and they act, like them, wholly at insensible distances, being confined in their exercise to the immediate surfaces of mutual contact of the opposed substances, and the compound formed at those surfaces becomes diffused through the fluid masses by capillary adhesion and mechanical mixture. This affords a reasonable explanation why fluidity of the receiving metal is essential to the formation of definite compounds at its surface, as well as why fluidity of the metallic salt is essential to its decomposition, and for the formation of definite compounds at the dissolving surface. If chemical action took place at sensible and considerable distances, *i.e.*, throughout the whole mass of the opposed fluid bodies, combination would probably be in all cases violent and instantaneous; and if fluidity were not essential to combination, the solid metals deposited upon the receiving surface would probably, in most cases, enter into the mass of the receiving metal, and combine with it.

27. **Alternation and Circulation of Chemical Affinities Necessary.**—The next chemical condition to be remarked upon is, that in every case of deposition the surfaces at which the acid and basic affinities are manifested *alternate* with each other in the circuit, and that the acid affinity *circulates* one way in the circuit, while the basic affinity *circulates* in the opposite direction; for instance:—

1st. *With One Metal and One Liquid.*—If we immerse a piece of copper in a solution of double cyanide of silver and potassium, it

becomes silvered; but if we immerse a piece of iron therein, it receives no deposit. In the first of these instances it is considered that, immediately upon the immersion of the metal, the superior affinity of copper for cyanogen over that of silver, causes it to combine with that substance, and set the silver free; at the same time, an immense number of minute currents of depositing force or chemical affinity are developed all over the immersed surface of the piece of copper, leaving it at innumerable minute points, passing a very small distance into the liquid, and re-entering the copper at numberless other points; and thus the affinities circulate, the copper dissolves, and receives a deposit simultaneously. In each of these atomic curcuits, as they are termed, acid affinity is exercised where the depositing force leaves the metal, and basic affinity where it re-enters it; but in the second instance, where iron is used, there is no circulation of those affinities, no dissolving of metal at one point, or deposition of it at another.

2nd. *With Two Metals and One Liquid.*—If we immerse a piece of iron and a piece of copper, in mutual contact, in a solution of sulphate of copper, a deposit of copper takes place upon the iron and upon the copper; but if we immerse a piece of gold in place of the iron, no

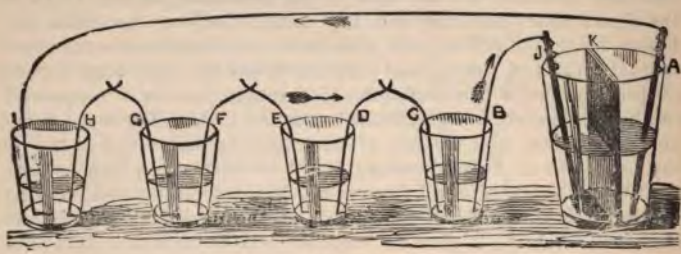

FIG. 17.

deposit occurs upon either. In the first of these instances, in addition to the circulation of atomic currents of affinity all over the immersed surface of the iron, as already explained, and which cause it to dissolve and receive a deposit, there is a separate and distinct current of the same force circulating through the liquid and the two metals at their points of contact, causing the surface of the iron to combine with the acid, and that of the copper to receive a metallic deposit; but in the second case there is no circulation of affinities, and no solution of the gold or deposition of the copper.

3rd. *With One Metal and Two Liquids.*—If we immerse two pieces of silver, one in a solution of cyanide of potassium, and the other in a

solution of double cyanide of silver and potassium, the two pieces being connected together by a wire, and the liquids touching each other by a porous partition, chemical affinities will circulate through the metals, wire, and liquids, and silver will be dissolved and deposited; but if we substitute pieces of iron for the pieces of silver, there will be no circulation of affinities and no deposition.

4th. *With Separate Depositing Liquids* (Fig. 17), consisting of solutions of sulphate of copper, with separate pairs of copper wire C D, E F, G H, immersed in them, and with end pieces of copper B and I, B being connected with a piece of zinc, J, immersed in dilute sulphuric acid, and I connected with a piece of copper, A, immersed in a solution of sulphate of copper, the two liquids being separated by a porous diaphragm, K, chemical affinities will circulate in opposite directions through the whole of the circuit, every alternate piece of immersed metal, J, I, G, E, and C, will exercise one kind of affinity and dissolve, whilst every other alternate piece, A, B, D, F, and H, will exercise an opposite kind of affinity, and receive a deposit of copper. If in either of the foregoing instances, where deposition occurs, we break the continuity of the circuit, either by separating the metals from each other at their points of contact, lifting them out of the liquid, or by cutting through the connecting wire, no deposition will occur; but if we immerse the free ends of the divided wire in a suitable liquid, such as a solution of sulphate of copper, if the wires are of copper, deposition will immediately recommence throughout the circuit.

FIG. 18.

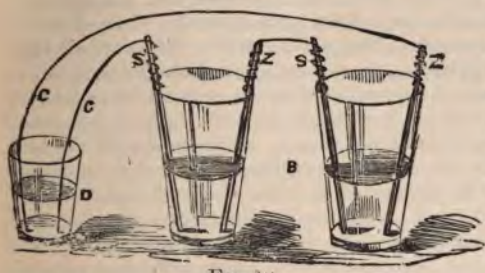

FIG. 19.

28. A consideration of such facts as these leads us to conclude that the process which causes every alternate metal in a series to combine

with *acids* and dissolve, and every other alternate metal in the circuit either to combine with bases, or receive a deposit, are of a chemical character, and *circulate* in opposite directions through the circuit, and has led to the application of the term "current affinity," to designate the depositing force, when viewed only in a *chemical* aspect.

29. Two or any other *even* number of vessels containing combinations of liquids and metals, each similar, and capable of generating current affinity, may be so arranged in a complete conducting circuit, that no such affinity will circulate or deposition occur; for instance, if we take two separate vessels, A and B (Fig. 18), each containing dilute sulphuric acid, and a separate piece of zinc, Z, and silver (S), and connect them together thus, zinc silver, silver zinc, no depositing power will be manifested if we immerse the free ends of their copper wires, C C, in a separate solution of sulphate of copper, D; but if they are connected thus, silver zinc, silver zinc (Fig. 19), and the copper wires immersed as before, current affinity will circulate and deposition will proceed in the separate liquid. In the first of these cases the affinities set in motion by the metals and liquid in the vessel A are opposite in direction to those generated in vessel B, and the two arrangements being equal in power, exactly neutralize each other, and prevent the currents of affinity and their effects: but in the second case the direction of the affinities evolved by the vessel A coincides with that of those from vessel B, the currents circulate, and deposition is effected. In the case of an unequal number of the metals of a series being connected the opposite way, those which are wrongly connected will neutralize and be neutralized by an equal number of the remainder, provided that all the pairs of metals and the liquids are similar; for instance, if three out of twelve are wrongly connected, they will neutralize the power of three more, and only the remaining six will act in the desired direction.

30. During the act of deposition, a salt is usually formed at the dissolving surface by the union of the metal with the acid elements of the liquid, and is dissolved in the liquid; at the same time the acid, which combines with the dissolving surface, is generally set free at the receiving surface by the deposition of the metal; for instance—

1st. *With One Metal and One Liquid.*—When iron coats itself with mercury by simple immersion in an acidulated solution of nitrate of mercury, nitrate of iron is formed by the union of the iron with the nitric acid, and nitric acid is at the same time set free from the salt by deposition of its mercury.

2nd. *With Two Metals and One Liquid.*—When copper receives a deposit of copper, by immersion in contact with a piece of iron in a solution of sulphate of copper, sulphate of iron is formed at the immersed surface of the iron, by the union of the sulphuric acid of the sulphate of copper

salt with the iron; at the same time sulphuric acid is set free at the copper surface by the deposition of the copper.

3rd. *With One Metal and Two Liquids.*—When copper receives a deposit of copper in a solution of sulphate of copper, by connection with another piece of copper immersed in dilute sulphuric acid, the two liquids touching each other by means of a porous partition or otherwise, sulphate of copper is formed at the surface of the metal in the dilute acid, by the union of the copper with the acid, and, at the same time, sulphuric acid is set free at the surface of the other piece by the deposition of the copper.

4th. *Silver.*—When silver or any other metal receives a coating of silver in a solution of double cyanide of silver and potassium, by connection with a piece of zinc in dilute sulphuric acid, the two liquids being separated by a porous diaphragm, sulphate of zinc is formed at the surface of the zinc, by the union of the acid and zinc, and cyanogen or hydrocyanic acid is at the same time set free at the receiving surface by the deposition of the silver.

5th. *With a Separate Depositing Liquid*, connected with any source of current affinity—for instance, when two silver plates, immersed in a solution of the double cyanide of silver and potassium, are connected by wires with a piece of zinc and a piece of copper immersed in dilute sulphuric acid in a separate vessel—cyanide of silver is formed at the surface of one of the pieces of silver by the union of that metal with the cyanogen of the liquid; and, at the same time, either cyanogen or hydrocyanic acid is set free at the surface of the other piece by the deposition of the silver.

31. **Proper Proportion of Free Acid in the Depositing Liquid.**—If a solution contains a large excess of uncombined acid, metallic deposition will not always occur; for instance, if two pieces of zinc are immersed in a neutral solution of sulphate of zinc, and connected by wires with another piece of zinc and a piece of silver immersed in dilute sulphuric acid in a separate vessel, one piece of zinc will dissolve and the other receive a deposit of metal; but if a rather large quantity of sulphuric acid is added to the depositing liquid, no deposit of zinc will occur. In the same manner, if we connect two pieces of silver, immersed in a strong solution of cyanide of potassium, with the zinc and silver in dilute sulphuric acid, as just described, one of the pieces of silver will combine with the cyanogen of the cyanide of potassium, and form cyanide of silver, which will combine with a portion of the remaining cyanide and then dissolve; but the other piece of silver will not receive a deposit of silver, until the remaining uncombined cyanide of potassium has decreased to a certain proportion by the working of the process. If, on the other hand, a depositing solution contains no *free* combining substance, deposition will either proceed very slowly, or be entirely

stopped, in consequence of an insoluble salt being formed upon the surface of the dissolving metal, and impeding the action; for instance, when two silver plates, immersed in a solution of double cyanide of silver and potassium, are connected with some source of depositing power, one of the plates will receive a deposit of silver, whilst the other will gradually become covered with a white layer of insoluble cyanide of silver, which impedes and eventually stops deposition.

32. **Necessity of a Proper Proportion of Water.**—If a depositing solution is diluted with water to a very large extent, deposition will progress very slowly, but if, on the other hand, it contains insufficient water, crystals of metallic salt will collect upon the dissolving metal and gradually stop the action; for instance, if two pieces of copper, immersed in a *saturated* solution of sulphate of copper containing free acid are connected with a piece of zinc and a piece of silver immersed in dilute sulphuric acid in a separate vessel, one piece will receive a deposit of copper, whilst the other will slowly dissolve and gradually become covered with crystals of sulphate of copper, first at its lower part and then at the edges, which will gradually stop the action.

33. All the foregoing chemical facts prove that chemical affinity plays a very important part in the phenomena of electro-deposition.

34. **Electrical Conditions of Deposition—Positive and Negative Substances Necessary.**—The first electrical condition to be observed is, that in every case of deposition the liquid contains both substances of an electro-positive and of an electro-negative character; metals and alkalies are electro-positive, and metalloids (oxygen, sulphur, chlorine, iodine, bromine, &c.) and acids are electro-negative; cyanogen is also electro-negative.

1st. *With One Metal and One Liquid.*—In the first instance, if we immerse a piece of copper in a solution of nitrate of mercury, deposition occurs, mercury being deposited, but if we immerse it in dry mercury, there is no deposition; in the former case the liquid contains both electro-positive mercury and negative nitric acid, but in the latter case it only contains the positive mercury.

2nd. *With Two Metals and One Liquid.*—Immerse zinc and platinum in mutual contact in a solution of nitrate of mercury, the platinum receives a deposit; but if we immerse them in dry mercury, it receives no deposit.

3rd. *With One Metal and Two Liquids.*—If one end of a platinum wire is immersed in a solution of cyanide of potassium, and the other end in a solution of nitrate of mercury, the two liquids touching each other through a porous partition, the end in the mercurial solution will receive a metallic deposit; but if dry mercury be substituted for the nitrate solution, no deposition will occur.

4th. *With Two Metals and Two Liquids.*—If we immerse zinc in dilute sulphuric acid, and platinum in a solution of nitrate of mercury, the metals touching each other, and the liquids separated by a porous partition, the platinum receives a mercurial deposit; but if dry mercury is substituted for the nitrate solution, no deposit occurs.

5th. *With a Separate Depositing Liquid*—If we immerse two platinum wires in a solution of nitrate of mercury, and connect them with any source of depositing power, one of the wires will receive a metallic deposit; but if we use dry mercury instead of the nitrate solution, there will be no deposit.

These and many other instances prove that unless the depositing liquid contains both electro-positive and electro-negative substances, no deposition occurs.

35. **Electric Polarity of the Dissolving and Receiving Metals.**—The second electrical condition to be observed upon is, that in every case of deposition there is an electrical difference between the dissolving and receiving metals, and that the former is always electro-positive, the latter being electro-negative, relatively to each other; the dissolving metal, consequently, has the strongest electrical attractions for the electro-negative or acid elements of the liquid, and the receiving metal has the strongest electrical attraction for the electro-positive or metallic elements; for instance—

1st. *With One Metal and One Liquid.*—Iron in a solution of sulphate of copper, being electro-positive to the copper of the salt, has a stronger electric attraction for the acid or electro-negative elements than the copper, and combines with them in setting the copper free; but in a solution of sulphate of zinc, iron being electro-negative to the zinc of the salt, has a weaker attraction for the acid than the zinc, and therefore does not combine with or set the zinc free.

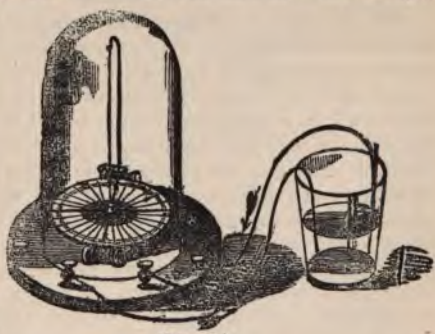

FIG. 20.

2nd. *Two Metals and One Liquid.*—If we immerse a piece of iron and a piece of copper in a solution of sulphate of copper, and connect them by wires with a galvanometer (Fig. 20), the copper will receive a deposit, and the needles N of the instrument will be strongly deflected in such a direction as to indicate that the iron is positive, and the

copper negative; but if a piece of iron and a piece of zinc are immersed in a solution of sulphate of zinc, and connected with the instrument, no deposit will take place upon either metal, and a much more feeble deflection will be produced.

3rd. *With One Metal and Two Liquids.*—If one piece of copper is immersed in dilute sulphuric acid, and another in a neutral solution of sulphate of copper, the two liquids touching each other by a porous partition, and the pieces of copper connected by wires with the galvanometer, deposition will take place upon the piece of copper in the metallic solution, and the instrument will indicate, by the direction of the deflection of its needles, that the dissolving piece of metal is positive, and the receiving piece negative; but if we substitute two pieces of platinum for the pieces of copper, no deposition of copper will occur, and only a feeble difference of electric condition between the two pieces of metal will be indicated by the galvanometer.

4th. *With Two Metals and Two Liquids.*—If a piece of zinc is immersed in dilute sulphuric acid, and a piece of copper in a solution of sulphate of copper, the two liquids being separated by a porous partition, and the metals connected with the galvanometer, deposition will take place freely upon the copper, and the needles of the instrument will be powerfully deflected, indicating, by the amount and direction of their movement, the zinc to be strongly positive and the copper negative; but if a piece of platinum is substituted for the zinc, there will be no deposition, and scarcely any deflection of the needles.

5th. *With a Separate Depositing Liquid.*—If we immerse two pieces of silver in a solution of the double cyanide of silver and potassium, and connect them with any source of depositing power, and interpose a galvanometer in the circuit, deposition of silver will occur, and the needles will be strongly deflected in such a direction as to indicate the dissolving piece of silver to be positive, and the receiving piece negative; but if we substitute two pieces of iron for the pieces of silver, there will be scarcely any deposition of silver, and very little deflection of the needles, the receiving piece being feebly negative. From these and many other similar cases we conclude that in every case where deposition occurs the dissolving metal is electro-positive, and the receiving metal electro-negative, relatively to each other, and that the former has the strongest electric attraction for the negative elements of the liquid, and the latter for the basic or metallic element. In all electric phenomena, positive substances repel positive and attract negative, and negative substances repel negative and attract positive.

36. **Alternation and Circulation of Electric-Polarities Necessary.**—The third electric condition is, that in every case of deposition the

positive and negative surfaces, or metals, *alternate* with each other in the circuit, and electric forces *circulate* through the circuit; for instance:—

1st. *With One Metal and One Liquid.*—When a piece of iron is immersed in a solution of sulphate of copper, innumerable minute electric currents are generated upon the surface of the metal, and circulate to a very minute depth within the opposed surface of the liquid; the positive electricity issuing out of innumerable points of the iron into the solution causes it to dissolve—passes through the solution, re-enters the iron at innumerable other points, and deposits the copper; but when a piece of gold is immersed in this solution, there are no currents of electricity generated, and the gold is neither dissolved nor does it receive a deposit.

2nd. *With Two Metals and One Liquid.*—When a piece of zinc and a piece of silver are immersed in mutual contact in a solution of nitrate of silver, the zinc dissolves and the silver receives a deposit, and an electric current is developed which circulates through the metals and liquids, and may be rendered further evident by connecting the metals with a galvanometer (Fig. 20); the zinc is positive and the silver negative.

3rd. *With One Metal and Two Liquids.*—When two pieces of copper are immersed, one in dilute sulphuric acid and the other in a solution of sulphate of copper, the two liquids touching each other through a porous diaphragm, and the pieces of copper connected with a galvanometer, an electric current circulates through the circuit, the piece of copper in the acid is positive and dissolves, and the piece in the metallic solution is negative and receives a deposit.

4th. *With Two Metals and Two Liquids.*—When a piece of zinc is immersed in dilute sulphuric acid, and a piece of silver in a solution of double cyanide of silver and potassium, and the two are connected with a galvanometer, the two liquids touching each other by a porous partition, electricity circulates through the circuit, the zinc is positive and dissolves, and the silver is negative and receives a deposit.

5th. *With a Separate Depositing Liquid.*—When two pieces of antimony, immersed in the ordinary chloride of antimony solution, are connected with any source of electricity, one piece becomes positive and dissolves, and the other negative and receives a deposit, and an electric current circulates through the circuit, as may easily be proved by the galvanometer, as in the foregoing instances.

6th. *With a Series of Depositing Liquids.*—If a series of depositing vessels (Figs. 15 and 17), containing solutions of sulphate of copper, and pieces of copper, are connected by their extreme pieces with a sheet of zinc and a sheet of copper immersed in a solution of sulphate of copper, every alternate piece of metal in the series will be electro-

positive and dissolve, and every other alternate piece electro-negative and receive a deposit, and a current of electricity will circulate through the whole series.

37. **Electrical Conducting Circuit Necessary.**—In every case where deposition is proceeding, the whole of the circuit is capable of conducting voltaic electricity; and this is one important condition of the result, for if in any such case we interpose an imperfect electric conductor in the circuit, such as a long iron wire, or a short column of water, the process will be greatly impeded, and if we interpose a non-conductor of electricity, such as a rod of gutta-percha, or allow the least film of air, dirt, or rust, to break the continuity of the circuit, deposition will be completely arrested.

38. **Electric Conductivity.**—The following is the general order of the conductivity of metals and alloys for voltaic electricity at 60° Fah., beginning with those which conduct most freely, viz., silver, copper, gold, cadmium, zinc, brass, tin, palladium, iron, steel, lead, platinum, german silver, antimony, mercury, bismuth, potassium. The order is somewhat different at other temperatures.

39. **Direction of the Electric Currents.**—In every case where a current of electricity is developed by the mutual contact of liquids and metals, or where it merely passes through them, as in a separate depositing vessel, the current of *positive* electricity is said to pass from the positive or dissolving metal, *through the liquid*, to the negative or receiving one; and the negative electricity to pass similarly in the opposite direction. When we speak of "*the current*," without stating what is meant,—the positive or negative electricity,—it is always intended, for the sake of simplicity of expression, to indicate the *positive* electricity; when we speak of the positive *metal* or *plate*, the metal which is positive and dissolves is meant; but when the positive *pole* is mentioned, the metal from which the positive electricity proceeds out of the arrangement or apparatus into the wires, and which is invariably the negative or receiving metal, is intended; for instance, if a piece of zinc and a piece of silver or copper are immersed in dilute sulphuric acid, the zinc is the *negative pole* and the *positive plate*, whilst the copper or silver is the *positive pole* and the *negative plate*.

40. In a separate depositing vessel it is the dissolving metal which is called the positive plate, because it corresponds to the zinc or dissolving plate of the battery, while the receiving metal is called the negative plate; the term pole is also sometimes applied to those plates, but in an irregular manner.

41. **Electrical Decomposition of Liquids.**—In all cases of electro-deposition, the elements of the liquids are split asunder by electric action at the surfaces of the metals; the electro-negative elements, such as metalloids and acids, either combine with, or are set free at

the surface of the dissolving or positive metal, and the electro-positive elements, such as metals and alkalies, either combine with, or are set free or deposited, at the surface of the receiving or negative metal; for instance, if a piece of silver and a piece of copper are immersed in a solution of sulphate of copper, and a piece of zinc and a piece of platinum immersed in dilute sulphuric acid, the silver connected with the zinc by one wire, and the copper with the platinum by another wire, the *negative* element of the liquid, namely, the sulphuric acid of the sulphate of copper solution, will be split from its associated copper, and will *combine* with the positive metal, the copper, causing it to dissolve in the liquid; while the *positive* element of the liquid, namely, the copper of the salt, will be deposited at the surface of the negative or receiving metal, the silver, but will not combine with it; but if we substitute a piece of platinum for the piece of copper, and mercury for the silver (Fig. 16), some of the effects will be reversed, the acid or negative element will collect around the positive platinum, but will not combine with it, whilst the positive element of the liquid, the copper, will be deposited and *combine* with the negative mercury. Fused salts usually yield the same substances by electric decomposition as the same salts yield dissolved in water.

42. **Electrical Terms in Deposition.**—To assist our remembrance of the different parts of the circuit and of the direction of the electric forces, and for the better understanding of the action of the currents, Faraday proposed the following terms, which have come into general use:—The liquid undergoing decomposition he termed an "*electrolyte*," from two Greek words, "electron," meaning "electric," and "luo," to "set free;" the act of electric decomposition he called "*electrolysis*;" the metallic or other surfaces at which the electric forces enter and leave a liquid he termed "*electrodes*," from two Greek words, "electron" and "odos," meaning a "way;" the positive electrode, or that point at which the positive electricity enters a liquid, is termed "*anode*," from two Greek words, "ana," meaning "upwards," and "odos," a "way,"—the way in which the sun rises; and the negative electrode, or that by which the positive electricity leaves a liquid, is termed "*cathode*," from two Greek words, "cata," meaning "downwards," and "odos," a "way,"—the way in which the sun sets; the elements of the liquid set free by electrolysis he termed "*ions*," from a Greek word meaning "going;" those which combine with, or are set free at the anode, are called "*anions*;" and those which combine with, or are set free at the cathode, are termed "*cations*."

43. **Anions and Cations.**—Under the head of Anions may be classed—oxygen, fluorine, chlorine, bromine, iodine, and cyanogen, probably also sulphocyanogen and the various mineral acids. Cations include—hydrogen (and ammonium), the alkali metals, magnesium, manganese,

arsenic, antimony, bismuth, zinc, cadmium, tin, lead, iron, cobalt, nickel, copper, mercury, silver, gold, platinum, palladium, and the salifiable bases.

44. **Electro-chemical Series.**—The various elementary substances have been arranged by Berzelius according to their relative degrees of positive and negative electro-chemical character, in a table or scale like the accompanying one, commencing with those substances possessing the strongest electro-positive properties, and ending with those of the strongest electro-negative properties:—

POSITIVE END.

NAME.	SYMBOL.
Caesium	Cs.
Rubidium	Rb.
Potassium	K.
Sodium	Na.
Lithium	L.
Barium	Ba.
Strontium	Sr.
Calcium	Ca.
Magnesium	Mg.
Glucinum	Gl.
Aluminium	Al.
Zirconium	Zr.
Cadmium	Cd.
Manganese	Mn.
Zinc	Zn.
Iron	Fe.
Nickel	Ni.
Cobalt	Co.
Cerium	Ce.
Lead	Pb.
Tin	Sn.
Bismuth	Bi.
Uranium	U.
Copper	Cu.
Silver	Ag.
Mercury	Hg.
Palladium	Pd.
Rhodium	R.
Platinum	Pt.
Iridium	Ir.
Osmium	Os.
Gold	Au.
Hydrogen	H.
Silicium	Si.
Titanium	Ti.
Tantalum	Ta.
Tellurium	Te.
Antimony	Sb.
Carbon	C.
Boron	B.
Tungsten	W.
Molybdenum	Mo.
Vanadium	Va.
Chromium	Cr.
Arsenic	As.
Phosphorus	P.
Selenium	Se.
Iodine	I.
Bromine	Br.
Chlorine	Cl.
Fluorine	F.
Nitrogen	N.
Sulphur	S.
Oxygen	O.

NEGATIVE END.

It may be observed that the division indicated in the above table between gold and hydrogen is, in a great measure, an arbitrary one; useful to assist one's memory in recollecting the general electro-chemical character of the substances, but not really existing in nature; for instance, sulphur and chlorine, two highly negative substances, must be viewed as positive in relation to oxygen. They are positive substances when combined with that element in hyposulphurous or hypochlorous acid, but are negative in relation to arsenic, hydrogen, zinc, potassium, when combined with those elements in the respective metallic sulphides and chlorides; in fact, each substance throughout the scale may be viewed as both positive and negative—positive in relation to those below it, and negative in relation to those above it; *those of the* upper end being strongly positive and feebly negative, and

those of the lower end strongly negative and weakly positive. It has been suggested that sulphur and nitrogen occupy a position too near the negative end of the scale, they being generally less negative than chlorine and fluorine; also that hydrogen should be placed higher up in the positive division.

45. A consideration of all the foregoing facts leads us to conclude that current electricity acts a most important part in all the phenomena of electro-deposition.

46. **Thermic Conditions.**—Under this head comparatively little can be said, because it is that portion of the subject which has been the least investigated; but it is manifest that, as heat is generally evolved by the chemical combination of metals with metalloids or with acids, there exists thermic as well as electric and chemical conditions of deposition. In a series of experiments with two plates of antimony immersed in a conducting liquid, the two plates being maintained at different temperatures, and numerous liquids being tried, a weak current of electricity was developed, which passed from the hot metal through the liquid to the cold one, the hot metal thus being positive. This occurred in all cases except with liquids containing uncombined nitric acid. Since the publication of the first edition of this book in 1856, thirty years ago, the thermal conditions of chemical and electro-chemical actions have been largely investigated, and may be briefly stated as follows:—

1st. The *decomposition* of a chemical compound into its constituents is attended by *absorption* of heat; whilst the *formation* of that compound by the union of those constituents is accompanied by *liberation* of heat. And 2nd. The decomposition of such a compound, whether by ordinary chemical action or by an electric current, absorbs exactly the same quantity of heat as that which is evolved by those ingredients whilst uniting to form that compound. Thus, the amount of heat absorbed by decomposing 18 grammes of water by means of the current, is the same as that evolved when 2 grammes of hydrogen and 16 grammes of oxygen are mixed together and caused to chemically unite by inflaming the mixture.

And as by the passage of an electric current through an aqueous metallic solution, chemical combinations or decompositions are continually produced at each electrode, heat is evolved or absorbed at those electrodes, and thermal changes constitute an important part of the phenomena of electro-deposition.

By passing an electric current through distilled water (containing sulphuric acid in order to make it conduct), by means of two pieces of platinum, chemical decomposition occurs at each electrode, and heat is absorbed at each; but on passing the current through a solution of sulphate of copper by means of two copper electrodes, chemical union

occurs and heat is evolved at the anode, whilst chemical decomposition, attended by absorption of heat, takes place at the cathode.

The quantity of heat evolved or absorbed in these actions is measured in units, termed calories. The usual unit employed is called the "gramme unit," and is the amount of heat required to raise the temperature of 1 gramme (or 15·432 grains) of water from 0° C. to 1° C.; or any other single Centigrade degree, say from 15° to 16° C.

The mode of stating, in writing, the amount of heat evolved (or absorbed) by the chemical union (or decomposition) of substances is as follows:—The chemical formulæ representing the two reacting substances are set down within a square bracket, the formula of the two substances being separated by a comma, and the number of units of heat evolved (or absorbed) is set down after the bracket, together with a plus sign to show that the heat is evolved and not absorbed; absorbed heat is indicated by a minus sign −. Thus, the formulæ $[H_2, Cl_2]=44000+$, indicates that 44000 units of heat (calories), or sufficient heat to raise the temperature of 44000 grammes weight of liquid water one Centigrade degree, are liberated when 2 atomic weights in grammes (*i.e.*, 2 grammes) of hydrogen and 2 atomic weights in grammes (or 71 grammes) of chlorine unite together chemically to form hydrochloric acid.

The formulæ used in thermo-chemistry represent the same relative weights of substances as in ordinary chemistry; thus $[Ag_2, O]$ represent 2 atomic weights of silver, each weighing 108, and 1 atomic weight of oxygen weighing 16. That of $[H_2O, SO_3]$ represents 1 molecular weight of water H_2O weighing 18, and 1 ditto of sulphuric anhydride SO_3 weighing 80. The atomic and molecular weights of a few substances are given in Sections 55 and 56.

There exist two additional thermic conditions of some importance attending electro-deposition. One of these is the heat evolved by the resistance which the mass of the liquid offers to the passage of the current through it—this is termed "heat of conduction-resistance"—and the other is the heat produced by the resistance offered to the passage of the current into and out of the liquid at the immediate surfaces of the electrode; this has been termed "heat of transfer-resistance." All substances resist in different degrees the passage of an electric current, and wherever the current passes through resistance it evolves heat. The conduction-resistance of nearly all metals is increased by rise of temperature, whilst that of aqueous solutions is diminished.

In addition:—If a U-shaped glass tube is half filled with any aqueous metallic solution, two perfectly similar pieces of the same metal, say platinum, connected with a galvanometer, their free ends then immersed in the liquid, the needles of the galvanometer allowed

to return to zero, and then the liquid in one of the limbs of the tube carefully warmed, an electric current is nearly always produced, and more frequently proceeds from the hot piece of metal through the liquid to the cold one than the reverse. (See *Proceedings* of the Royal Society, 1884, pp. 251-290.)

47. **Influence of Temperature on the Depositing Liquid.**—The strength of affinity between the different elements of a liquid undergoing electrolysis varies with the temperature of the liquid, and is almost invariably diminished by elevation of temperature. Rise of temperature increases the electric conductibility of an electrolyte, and decreases that of the metal plates immersed in it; but the decrease of conductibility of the latter is small in proportion, at moderate elevations of temperature, compared with the increase of the former; consequently, the general effect of heating a depositing liquid is to increase the rapidity of deposition.

48. We have repeatedly observed, that with some solutions used at a high temperature for depositing, if the cathode was immersed in the liquid at the ordinary atmospheric temperature, and the liquid then heated to the desired point, no conduction or deposition took place; nor did it occur if the receiving metal was taken out, washed in cold water, and re-immersed; but if the temperature of the liquid was first raised, and then the cold cathode suddenly immersed, deposition took place freely, and the liquid might be cooled down many degrees without stopping the action. In coating iron with tin in some solutions, if the iron was immersed before heating the liquid, no deposition took place, even at 150° Fah.; but if the liquid was first heated, deposition occurred below 100° Fah.

49. **Influence of Light upon Deposition.**—Light appears to exercise much less influence than heat upon electro-deposition; in some cases however, where the elements of a depositing liquid are held together by unstable affinities, it decomposes the liquid and renders it unfit for deposition; for instance, a solution formed by dissolving hyposulphite of silver in a solution of hyposulphite of soda has a tendency to be decomposed in this way.

50. **Dynamic or Mechanical Conditions.**—The various phenomena occurring in a liquid undergoing electrolysis, may be viewed, in a mechanical or dynamic aspect, as a series of minute movements (attractions and repulsions) occurring between the various particles of matter composing the opposed surfaces of the liquids and of the metals immersed in them; for instance, if we immerse a piece of zinc in a solution of sulphate of copper and connect it with some mercury in the same liquid, by a platinum wire protected from the solution by a tube of glass or gutta-percha, the particles composing the surface of the zinc, being all electro-positive, will tend to repel each other,

and the particles of the liquid surface in contact with it, being rendered electro-negative, will also tend to repel each other, whilst the particles of acid near, being electro-negative, will attract the particles of zinc, which are electro-positive, and the two will combine together and form a salt; at the same time, the particles of the liquid surface in contact with the mercury, being made electro-positive, will tend to repel each other; while the particles of the opposed mercury surface, being rendered electro-negative, will also tend to repel each other; whilst the particles of the mercury, being electro-negative, and the contiguous particles of copper in the liquid being electro-positive, the two will combine together and form an alloy. The deposition of copper upon the *zinc* in this case must be wholly disregarded, because it is quite a separate and distinct phenomenon, due to minute local currents.

To put this in a clearer form, suppose (Fig. 21) the vertical row of particles Cu, Cu, Cu, Cu, to represent the copper anode of a sulphate of copper depositing liquid, and the row of particles Hg, Hg, Hg, Hg, the mercury cathode, Pt, Pt, being the connecting wires from the battery, and the double row representing the particles of acid SO_4, and copper Cu', composing the intervening liquid; the particles of the anode surface, being all electro-positive, tend to repel each other; and the contiguous particles of Cu' and SO_4, being all negative, also tend to repel each other, whilst the particles of the copper anode, being positive, attract the nearest particles of negative acid, and combine with them and form a salt; at the same time, the particles of Cu' and SO_4 nearest the mercury, being all positive, tend to repel each other, whilst the contiguous particles of mercury being negative, and the copper in the liquid being positive, attract and combine with each other and form an alloy. By this combination of simultaneous movements, the copper anode dissolves, and the mercury (or any other conducting substance which forms the cathode) receives a deposit, and the particles of copper of the liquid are gradually removed and replaced by those from the anode.

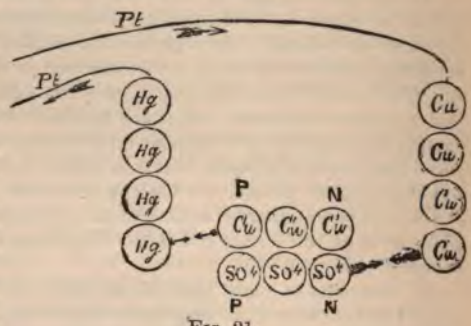

FIG. 21.

51. These attractions and repulsions, like ordinary chemical actions, are all supposed to take place at insensible distances, at the mutually opposed surfaces of the liquids and metals, and not to extend into their masses, except so far as they are mixed with each other by capillary attraction or ordinary mechanical motion, and can therefore only take place where one or both of the substances are in a liquid state; if it were otherwise, the combinations and decompositions of the whole masses would probably occur instantaneously.

52. In addition to those minute and invisible movements of the particles, there are other and sometimes visible movements produced by capillary attraction and by difference of specific gravity in the liquids; for instance, the salt formed at the anode, if it is soluble in the liquid, is dissolved and gradually diffused through it by capillary attraction or adhesion, whilst from its greater specific gravity than the remainder of the liquid when dissolved, it tends to sink towards the bottom; at the same time, the acid set free at the cathode is likewise gradually diffused through the liquid by similar means, and from its less specific gravity tends to rise to the surface. These movements are of general occurence during deposition, and in some solutions, especially if they are very dense and possess a colour, are plainly visible to the unassisted eye; and their occurrence explains why the substances set free by deposition are not instantaneously transferred from one electrode to the other, but occupy, especially in dense liquids and with electrodes far apart, a considerable period of time in their transference; it also explains why, if depositing solutions are not occasionally stirred, their upper portions become exhausted of metal, whilst their lower parts become deficient of acid. Motion of the cathode is generally considered necessary to make the deposited metal harder.

53. **Position of the Electrodes.**—The position of the electrodes has considerable influence upon the phenomena of electro-deposition. For instance—1st, If the two electrodes in a depositing liquid are horizontal, with the anode above and the cathode below, the salt formed at the anode will, by virtue of its greater specific gravity, sink in the liquid, whilst the acid set free at the cathode will, by its less specific gravity, rise upwards, and thus the anode will be constantly supplied with fresh uncombined acid, the cathode will receive a constant supply of metallic salt, and deposition will continue without interruption. 2nd, If the two electrodes are vertical in the liquid, and opposite to each other, similar differences of specific gravity will cause the lower part of the liquid to become saturated with metallic salt, and its upper part to consist of free acid mixed with the water; in consequence of this, the current of electricity will almost wholly pass from the upper part of the anode diagonally downwards through the liquid, to the lower part of the cathode, and thus the upper part of the anode will

dissolve rapidly, whilst its lower part will dissolve but slowly, and the cathode will receive a rapid deposit at its lower part and but very little at its upper part. In this position, vertical lines, and even deep grooves, are sometimes produced in the deposit (especially if the upper part of the cathode slightly overhangs) by the ascent of streams of the lighter acid liquid from which the metal has been exhausted by deposition; if the solution is nearly a saturated one, and has been freely worked without stirring or disturbance for some time, crystals of the metallic salt are apt to form all over the lower part of the anode, which will be dissolved very rapidly at the surface of the liquid, and appear as if cut by a knife; in addition to these effects, if the solution is a very deep one, with much free acid, two independent currents of electricity will be developed, one in each electrode, by the unequal action of the two different strata of liquid upon their upper and lower parts. An instance of this will be found in "One Metal in Two Liquids,"(9), in which these currents leave them at their upper parts, pass down through the liquid, and re-enter them at their lower extremities.

54. **Form of the Electrodes.**—If either of the electrodes be of an irregular form, or have unequal projections or hollows, the anode will dissolve most freely, and the cathode receive the greatest deposit of metal at those parts at which they are nearest each other, and least in the hollows and more distinct parts. If the surface of the cathode be rough, it greatly increases the tendency of the deposit to become crystalline.

55. **Mathematical Conditions.**—*Definite Chemical Action.*—In the combination of different elementary and compound substances with each other, by ordinary chemical affinity, it has been observed, and accurately proved by analysis, that their combinations invariably take place in certain definite proportions, or in very simple multiples of those proportions; and as in the first of these cases it is inferred that their combinations with each other occur, one atom with one atom, the numbers which represent those proportions represent also the relative weights of those atoms to each other. The following table contains the names, symbols, and atomic weights of nearly all the known simple or elementary substances:—

Name.	Symbol.	Atomic weight.	Name.	Symbol.	Atomic weight.
Aluminum	Al	27·0	Boron	B	10·9
Antimony	Sb	120·0	Bromine	Br	80·0
Arsenic	As	75·0	Cadmium	Cd	112·0
Barium	Ba	137·0	Caesium	Cs	133·0
Beryllium	Be	9·0	Calcium	Ca	40·0
Bismuth	Bi	207·0	Carbon	C	12·0

Name.	Symbol.	Atomic weight.
Cerium	Ce	141·0
Chlorine	Cl	35·5
Chromium	Cr	52·5
Cobalt	Co	59·0
Copper	Cu	63·5
Fluorine	F	19·0
Gallium	Ga	69·8
Gold	Au	196·5
Hydrogen	H	1·0
Indium	In	72·0
Iodine	I	127·0
Iridium	Ir	197·0
Iron	Fe	56·0
Lead	Pb	206·5
Lithium	Li	7·0
Magnesium	Mg	24·3
Manganese	Mn	55·0
Mercury	Hg	200·0
Molybdenum	Mo	96·0
Nickel	Ni	59·0
Nitrogen	N	14·0
Osmium	Os	199·0
Oxygen	O	16·0
Palladium	Pd	106·5
Phosphorus	P	31·0
Platinum	Pt	197·0
Potassium	K	39·1
Rhodium	Ro	104·0
Rubidium	Rb	85·0
Ruthenium	Ru	104·0
Selenium	Se	79·5
Silicon	Si	28·0
Silver	Ag	108·0
Sodium	Na	23·0
Strontium	Sr	87·5
Sulphur	S	32·0
Tellurium	Te	129·0
Thallium	Tl	204·0
Tin	Sn	118·0
Titanium	Ti	50·0
Tungsten	W	184·0
Uranium	U	240·0
Vanadium	V	51·0
Zinc	Zn	65·0
Zirconium	Zr	90·0

56. As there are a number of compound substances used in electro-deposition, such as sulphuric acid, cyanide of potassium, &c., and it will be useful to the practical depositor to know their combining proportions in making the different salts used in the art, we have selected those which are likely to be required, and give their names, symbols, and molecular weights:—

Water, $H_2O=18$.

Sulphuric Acid (Oil of Vitrol), sp. gr., 1·848; $H_2SO_4=98$.

Hydrochloric Acid (Spirit of Salt), sp. gr., 1·21; $HCl, 3H_2O=90·5$.

Nitric Acid (Aqua-Fortis) sp. gr., 1·52; $HNO_3=63$.

Carbonate of Ammonium (Sal-volatile) = 236.

Chloride of Ammonium (Sal-ammoniac), $H_4NCl=53·5$.

Caustic Lime, $CaO=56$.

Calcined Magnesia, $MgO=40$.

Carbonate of Magnesium, $MgCO_3=84$.

Oxide of Zinc, $ZnO=81$.

Sulphate of Zinc (White Vitrol) $ZnSO_4+7H_2O=287$.

Red Oxide of Iron (Jewellers' Rouge) $Fe_2O_3=160$.

Sulphate of Iron (Green Vitrol), $FeSO_4+7H_2O=278$.

Black Oxide of Copper, $CuO=79·5$.

Oxide of Silver, $Ag_2O=232$.

Sulphate of Copper (Blue Vitrol), $CuSO_4+5H_2O=249·5$.

Chloride of Silver, $AgCl = 143{\cdot}6$.
Hydrate of Potassium (Fused Caustic Potash), $KHO = 56{\cdot}2$.
Carbonate of Potassium (Pearl Ash), $K_2CO_3 = 138{\cdot}2$.
Carbonate of Sodium (Washing Soda Crystals), $Na_2CO_3 + 10H_2O = 286$.
Chloride of Sodium (Common Salt) $NaCl = 58{\cdot}5$.
Nitrate of Silver, $AgNO_3 = 170$.
Oxide of Gold, $Au_2O_3 = 441{\cdot}2$.
Chloride of Gold, $AuCl_3 = 303$.
Chloride of Platinum, $PtCl_2 = 268$.
Cyanogen, $Cy = 26$.
Cyanide of Potassium, $KCy = 65{\cdot}2$.
" " Zinc, $ZnCy_2 = 117$.
" " Copper, $Cu_2Cy_2 = 204$.
" " Mercury, $HgCy_2 = 251$.
" " Silver, $AgCy = 134$.
" " Gold, $AuCy_3 = 274{\cdot}5$.

Unless the student possesses a sufficient amount of knowledge of chemistry, he will not be able to use the Tables of Atomic and Molecular Weights with perfect success. In order to fully understand those tables he must be able to read and interpret chemical formulæ, and know the meanings of the terms—atomic and molecular weight, combining proportions, equivalent weight, atom, molecule, monad, dyad, triad, monobasic, bibasic, &c., and to acquire this ability he should receive chemical instruction.

57. **Definite Electro-Chemical Action.**—The chief mathematical condition of electro-deposition is, that in every case, all the actions, both of combination and decomposition, take place in certain definite proportions—that is, according to the relative equivalent weights of the substances, combining or being decomposed. For instance:—

1st. *With One Metal and One Liquid.*—If a piece of pure iron is immersed in a solution of sulphate of copper, it is dissolved, and copper is deposited; and for every 56 parts, or one atomic combining proportion of iron dissolved, 63·5 parts, or one atomic weight of copper are deposited, and 98 parts (one equivalent) of hydrate of sulphuric acid (common oil of vitrol) are separated from the copper, and combine with the iron, forming therewith one equivalent of protosulphate of iron.

2nd. *With Two Metals and One Liquid.*—If a piece of zinc and a piece of silver in mutual contact are immersed in a solution of nitrate of silver, the zinc will dissolve and the silver receive a deposit; and for every 216 parts of silver deposited, 65 parts of zinc will be dissolved.

3rd. *With One Metal and Two Liquids.*—If one piece of copper is immersed in a solution of sulphate of copper, and another in dilute sulphuric acid, the two being connected together by a wire, and the liquids touching each other by a porous partition, copper will be dissolved in the dilute acid in the proportion of 63·5 parts for every 63·5 parts of copper deposited in the metallic solutions; and for every 98 parts, or one equivalent, of hydrate of sulphuric acid set free at the

cathode by the deposition of the equivalent of copper, one equivalent of acid will combine with a like amount of copper at the anode.

4th. *With Two Metals and Two Liquids.*—If we immerse a piece of zinc in dilute sulphuric acid, and a piece of silver in a solution of double cyanide of silver and potassium, the two metals being connected by a wire, and the liquids touching each other by a porous partition, one equivalent, or 65 parts, of zinc will combine with one equivalent of the acid, and one equivalent, or 216 parts, of silver will be deposited, setting one equivalent, or 26 parts, of cyanogen free.

5th. *With a Separate Depositing Liquid.*—If the plates of a battery are connected by wires with two pieces of gold in a hot solution of double cyanide of gold and potassium, for every atomic equivalent, or 196·5 parts of gold deposited, and one equivalent of cyanogen set free, one equivalent of gold will combine with one equivalent of cyanogen, and dissolve; and not only this, but for each of these actions one equivalent of zinc will combine with one equivalent of acid, and one equivalent of hydrogen will be evolved in each of the battery cells supplying the current of electricity.

6th. *With a whole Series of Depositing Liquids.*—Such, for instance, as solutions of sulphate of copper with electrodes of copper,—arranged as in Figs. 15 and 17,—connected with a piece of zinc immersed in dilute sulphuric acid, and a piece of copper immersed in a solution of sulphate of copper, the last two liquids touching each other by a porous diaphragm, the whole of the combinations, decompositions, and depositions throughout the series, will occur in the proportions of their molecular weights or chemical equivalents. These, and many other instances which might be adduced, prove that all the electro-chemical actions taking place in any given circuit occur in certain definite proportions, and that this definite electro-chemical action is one very important condition of electro-deposition.

58. **Binary Theory of Electrolysis.**—This law of definite electro-chemical action was first established by Faraday, and in addition he advanced what is termed the binary theory of electrolysis—that "only those compounds of the first order are *directly* decomposable by the electric current which contain one atom of one of their elements for each atom of the other; for instance, compounds containing one atom of hydrogen or metal with one atom of oxygen, iodine, bromine, chlorine, fluorine, or cyanogen;" whilst "boracic acid (BO_3), sulphurous acid (SO_2), sulphuric acid (SO_3), iodide of sulphur, chloride of phosphorus (PCl_3) and (PCl_5), chloride of sulphur (S_2Cl), chloride of carbon (C_4Cl_6), bichloride of tin ($SnCl_2$), terchloride of arsenic ($AsCl_3$), quintochloride of antimony ($SbCl_5$)," are non-conductors of electricity, and incapable of electrolysis. Some substances, which are not of the simple binary character mentioned,

are decomposed by current electricity, and yield their positive and negative elements in equivalent proportions at the respective electrodes; but, according to this theory, they are *indirectly* decomposed, *i.e.*, they are decomposed by the chemical action of some of the elements set free by the direct action of the current upon other substances present. For instance, "fused borax (biborate of soda NaO, $2BO_3$) yields oxygen gas at the anode and boron at the cathode; now, since fused borax is not decomposable by the electric current, the separation of the boron must be attributed to indirect action; the current resolves the soda (NaO) into oxygen and sodium, and the latter separates boron from the boracic acid"—(*Faraday*). Again, an aqueous solution of ammonia (HO,NH_3) yields, by electrolysis, nitrogen gas at the anode and hydrogen at the cathode. In this case, according to the theory, it may be supposed that only the water (HO) is *directly* decomposed, and that its oxygen, set free at the anode, combines chemically with some of the hydrogen of the ammonia, again forming water, and thus indirectly its nitrogen is set free.

59. **Mathematical Idea of Electro-depositing Force.**—A consideration of the law of definite electro-chemical action, and the binary theory of electrolysis, leads us to view the electric current or depositing force in a mathematical aspect, as "an axis of forces equal in power, but opposite in direction," because, for every atom of an electro-positive substance attracted or transferred in one direction, an equivalent of negative substance is attracted in the opposite direction. It also suggests to us the idea that an intimate connection exists between those equivalents or mathematical relations of matter and the development of current electricity by chemical action, and its transference through liquids by electrolysis, because these phenomena only occur when the mathematical conditions are present.

60. **Sizes of Electrodes, Liquids, and Wires.**—The rapidity of deposition is influenced by the area of the electrodes, the length and section of the intervening liquid, and of the connecting wire; the larger the immersed surfaces of the metals, the shorter the length and the greater the transverse area of the liquid between them, and the shorter and thicker the connecting wire, the more rapid is the process of deposition. If the anode is very large and immersed in the lower part of the liquid, and the cathode very small and suspended near the surface, much more metal will be dissolved than is deposited, gas being generally evolved at the cathode in place of some of the metal deposited.

61. **Rapidity of Deposition.**—The character of the deposited metal is very much influenced by the rapidity of deposition: if it is deposited very rapidly, it will be in the state of a perfectly black, soft, non-coherent powder; if deposited more slowly, it will possess the ordinary

characters of the particular metal; and if deposited very slowly, it will be crystalline, because the atoms are then allowed sufficient time to arrange themselves in the crystalline form.

62. **Logical Conditions.**—The logical conditions are—1st, that there is a *difference* at the dissolving and receiving surfaces, either in the "*material substratum*" of metal, of liquid, in the *forces* involved, or in all combined, both of chemical affinity and electricity, probably also of heat and of motion; and, 2nd, that in all cases of deposition there are certain chemical, electrical, thermic, dynamic, and mathematical conditions invariably present, and certain other conditions of each of those kinds invariably absent, both of which classes of conditions are necessary to the production of the phenomena; the whole of the necessarily present circumstances constituting its causes, and all the necessarily absent ones constituting its preventives; thus, if *all* the causes of deposition are present, and *all* its preventives absent, deposition will invariably occur; but if only one of its causes is absent, or one of its preventives present, deposition cannot take place.

63. **Ontological Condition.**—The last, the most necessary, most evident, and most simple condition of all deposition is—that metals, liquids, and forces are required in order to produce it. For a more complete exposition, however, of the principles and facts upon which all electro-deposition depends, the student is recommended to consult a small book on "Electro-Chemistry."*

THE PRACTICE OF ELECTRO-DEPOSITION.

64. **Objects of Practical Deposition.**—In the theoretical division we have brought forward a large number of instances, both of deposition and non-deposition; and from a consideration of them we have drawn conclusions both as to what substances and what conditions and arrangements of those substances really exist in all cases of deposition, and in simliar cases of non-deposition; and we have pointed out in what respects the conditions varied. Our object in pursuing this course was to impress the reader with a fuller knowledge of the theoretical principles on which deposition depends, in order that he may be better able to apply his knowledge to remove difficulties which arise in his practice. Now, however, our object is different; it is to instruct the reader how to apply those principles in daily working, to give him practical rules, recipes, and directions for carrying out the various minute points in workshop manipulation; and to enable him to obtain the greatest degree of practical success.

65. **General Arrangement of Apparatus, &c.**—The practical part will be best arranged by beginning at the very commencement; and

* Written by the same Author.

assuming the reader to be without materials or apparatus of any kind—that he has to provide a workshop, prepare his solutions, batteries, scouring and cleaning apparatus; that he has to clean his articles for receiving deposits, and prepare his materials for moulds, before he can commence the process of deposition, gradually acquiring a knowledge, as he proceeds, of the kind of depositing process best fitted for his purpose; of the most suitable source of depositing power; the best solutions; the best methods of making solutions; the construction of voltaic batteries and of dynamo-electric machines; the rules for regulating the currents of electricity, and the character of the deposited metals; rules for depositing metals generally, as well as for cleaning and preparing metal articles to receive deposits; copying works of art by moulding; preparation of moulds for receiving deposits; making solutions for ordinary coppering, silvering, and gilding; and for the management of those solutions;—information on all these points it will be our task to supply.

66. **First Considerations.**—The first step in practice is, to consider the probable magnitude of the operations to be carried on, and to provide rooms of suitable size. These should be upon the ground floor (except for electro-gilding), well lighted and ventilated, with conveniences for the erection of boilers and drying flues, for placing washing troughs, depositing vats and batteries, and for the escape of unwholesome vapours; there should also be ready access to a plentiful supply of clean water. The establishment should consist of at least three rooms, and an open yard with an outhouse; an upper or more private room for gilding, a ground-floor room for silvering, and another ground-floor room for the coarser work, such as coppering, brassing, and the preparation of the larger and coarser articles for receiving deposits. The outhouse is for the batteries, and the yard for washing the battery cells. If a dynamo-electric machine is employed, an additional small, dry, and clean apartment will be required, which should be reserved for it alone.

67. **Boilers, Furnaces.**—For the purpose of general deposition, several large iron boilers, with furnaces beneath, either in the coppering room or in close proximity to the silvering-room, are required; these are to contain solutions of caustic potash for cleaning articles. A low furnace should be erected between those rooms, having a long horizontal flue covered with plates of iron, for drying deposited or plated articles upon; the room for coppering should be furnished either with a low furnace or stove for heating the solutions used for coppering or brassing iron. Each room, whether for coppering, silvering, or gilding, should be provided with a tap of running water, and a leaden trough beneath, for washing the smaller articles; and the coppering-room should be furnished with one or two large wooden tubs

or troughs, filled with water, for washing articles of larger size; both this room and the outhouse should contain a number of large stone-ware pans and jars, oval and round, of different sizes and proportions, to contain the various "pickling" and "dipping" liquids, acids, or "spent solutions." Several large iron trays, filled with sawdust, should also be provided and fitted upon the furnace flue, for drying plated and deposited articles upon. Each of the rooms should be provided with a "scratch-brush lathe," for scouring the various articles. The gilding-room should have several small stoves for heating gilding solutions, or, in lieu thereof, several iron tripods, with Bunsen burners beneath. The silvering and coppering-rooms should each be provided with one or two pairs of large and well-insulated copper wires, proceeding from the depositing vats to the batteries or dynamo-machine. The gilding-room will not require these, small batteries only being used in it, which are kept in the same room.

68. **Sources of Electricity.**—A point for early consideration will be whether a dynamo machine or batteries shall be used as the source of generating energy. The choice will depend very much upon the amount of work to be undertaken; if the quantities of materials to be operated upon are large, then the dynamo is the most economic; if small, and the work is carried on only at intervals, then batteries may be more convenient. The question of a dynamo also involves that of motive power and space. Small gas engines or petroleum engines may prove more satisfactory than steam engines, especially in small factories, but a great convenience will be gained when the system of distributing power is carried out in our large towns either by hydraulic or electrical mains through the streets.

69. **Construction of Dynamo Machines.**—The simplest form of apparatus for generating current electricity by the joint influence of magnetism and motion has been already described (§ 15), but the apparatus required for practical work is far more elaborate and costly in its construction. If we take a magnet we find that it will exercise a directive influence over certain materials, such for example as iron filings, so that if a sheet of paper is laid or held immediately over a magnet, and iron filings be sprinkled upon the paper the filings arrange themselves symmetrically under the action of the magnet and form a series of closed curves from one point of the magnet to another point. These points are near the ends of the magnet and are called its poles. It is also found that the influence of the magnet decreases with the distance from the poles; and the whole area over which the influence is excited is called the "magnetic field." The lines in which the iron filings arrange themselves under the influence of the magnet are called the "lines of magnetic force" or shortly "lines of force." The strength of a magnetic field depends upon the number of "lines of

force" per unit area in that field. It is found that when a conductor, such as a copper wire, is moved into a magnetic field, so that the lines of force are cut through by the conductor, an electric current is generated during its motion. It is also noticed that a wire thus moved across the lines towards one pole of the magnet has generated in it a

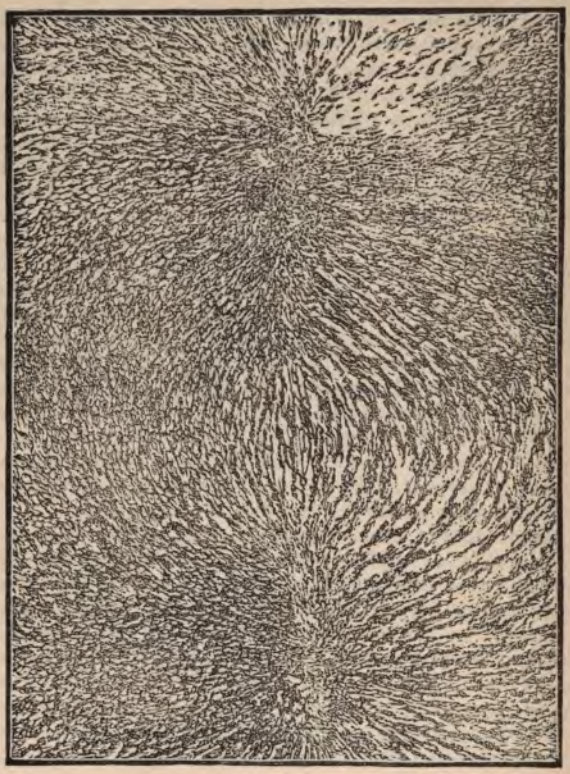

FIG. 22.—ARRANGEMENT OF IRON FILINGS UNDER ACTION OF MAGNET.

current seemingly opposite as regards direction to the current generated when approaching the other pole of the magnet. The object of modern constructors of dynamos has been to obtain a very strong magnetic field by means of electro-magnets, and to rotate copper wire circuits wound upon iron through this field. This rotating part is called

the armature. The electro-magnets (field magnets) are so arranged as to bring the opposite poles as near each other as possible, allowing space for the armature to rotate between, and as each coil of the armature in each rotation passes in front, first of one pole, then of the other, the current generated in the coil alternates in direction. For certain purposes such alternating currents can be utilised as generated, but they are not applicable for purposes of electro-deposition. An addition is therefore made to the machine to collect the currents,

FIG. 23.

throw them into one uniform direction, and convey them to the depositing vat. This is the commutator, which is shown in a simple form in Fig. 23. Two springs or brushes (DE) press against the commutator (C), which, in Fig. 23, consists of four quadrants of copper or brass mounted on the same axis, but insulated from it, and from each other. The brushes and quadrants are so arranged at their points of mutual contact that, just at the moment that the currents are changed in direction by the armature passing the magnet, the revolution of

FIG. 24.

COMMUTATOR—SIDE VIEW. COMMUTATOR—SECTION.

the axle causes the points of contact of the springs to pass from one quadrant to the other; and thus, by reversing the connection at the moment the direction of the current is changed, an uniform direction of current is obtained in the wires beyond. This action will be better understood by an examination of Fig. 24. In a dynamo, the complete conductive circuit is made up of the armature coil, the two ends of which are connected to commutator bars, and from the bars, by brushes, to an external circuit. Fig. 24 shows this in a simple form.

A is the rotating axle or shaft of the dynamo, upon which are two commutator bars (P, P′) of brass or copper, insulated from the axle, and from each other. In an actual machine there are usually a number of armature coils, and a corresponding number of commutator bars, and not two only, as shown in these diagrams. The external connection between P and P′ is made by means of the brushes B, C pressing upon P and P′ respectively, these brushes being connected by wire or other conducting material, such as a depositing liquid. The armature coil, or the internal part of the circuit, has its ends D, D′ connected to the bars P, P′. The action to be considered is a follows:—The armature coil whilst being rotated in the magnetic field has a current generated in it, say, in the direction D to D′. Let us trace this current through the complete circuit, that is through the internal and external portions commencing at D. The arrows ——> show the direction to D′, from D′ the current goes to the brush C, through the external wire E E, the depositing vat V to the brush B, and the bar P to the starting point D. This completes one action. Now, consider the axle rotated through 180°, the position of the bars P and P′ will be reversed, but, for the purpose of simplifying the explanation, we will suppose the brushes B and C reversed to B′ and C′. In the new position the current in the armature coil is from D′ to D, as shown by the arrows ——>-> from D to the commutator bar and to the brush C′, from whence through the external circuit *in the same direction as before* to B′, thus showing that, although the direction of the current is reversed in the internal part of the circuit, the direction is unaltered in the external portion.

The dynamo (Fig. 25) has been designed by Prof. G. Forbes especially for depositing purposes, and consists essentially of a revolving mass of iron, which may be called the armature. It may be a disc or a solid cylinder. The latter is best. Round the middle of the circumference of this revolving mass a circular coil of iron is wound. It does not revolve, but remains fixed. The cylinder is placed inside an iron casing, which may be called the field magnets. This casing and the armature enclose the wire coil. The casing is fixed to a bed-plate. An electric current sent through the wire-coil magnetizes the machine. The wire is in an annular space. One of the collectors must be inside this annular space and one must be outside, and both must rub on the revolving cylinder of iron. The arrangement of brushes varies in different types. The machine described is suitable for 2 volts to 6 volts, giving currents from 10,000 amperes to any required amount, depending on the size of machine. A machine with two discs, fitted at Philadelphia, Pa., in 1884, gave 5·8 volts. It only gave 3,117 amperes, because the discs have more resistance than a solid cylinder. Designs

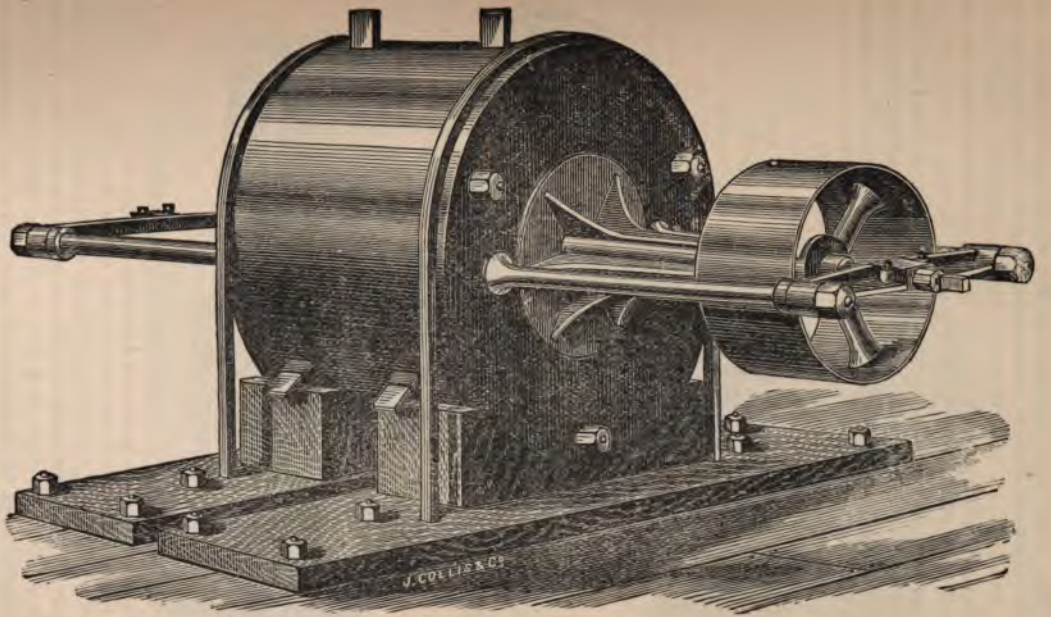

FIG. 25.—THE FORBES NON-POLAR DYNAMO FOR DEPOSITING PURPOSES.

have been made for compounding the effect, and increasing the E.M.F. This machine has no commutator, and no waste magnetic field, and may be said to be a simple practical adaptation of Faraday's original experiment to obtain a current from a disc revolving between the poles of a magnet.

Fig. 26 shows a machine of the Gramme type, designed and built by Messrs. R. E. Crompton & Co., for electro-deposition. This firm prefers machines of a moderate, rather than a very low, electromotive force.

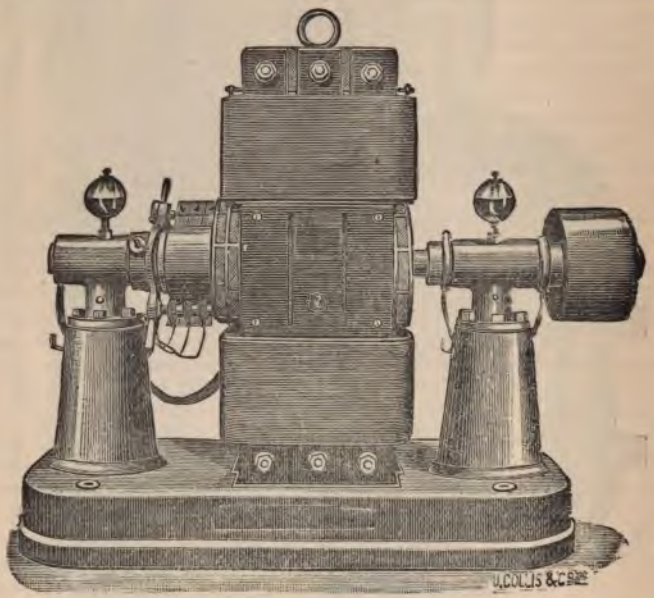

FIG. 26.

A moderate E.M.F. is convenient and economical, as the cost of the connecting wires increases with the lowness of the E.M.F. In machines giving very large currents the armature conductors, which sometimes take the form of copper bars, are apt to get very hot from local or Foucault currents, In the machine shown in Fig. 26 this source of loss is obviated by a new method adopted in the winding. Each conductor on the outside of the armature is split into two; that is to say, instead of a large bar, two smaller bars are laid side by side.

These cross one under the other half-way along the armature. A groove is turned in the armature to allow room for the crossing. This prevents the Foucault currents, as the electromotive force in each of the two bars is the same, and there is no tendency for a current to go along one and back again by the other, as there would be if the two bars were merely laid side by side, instead of crossing one under the other. Fig. 27 shows a Victoria dynamo as constructed by the Anglo-American Brush Electric Light Corporation for electro-depositing purposes. This machine may also be said to be of the Gramme type, but with a flattened ring or disc armature in place of the ring armature.

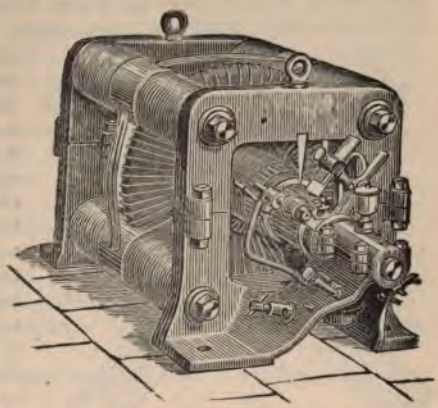

FIG. 27.—THE VICTORIA DYNAMO.

Fig. 28 shows another type of machine also constructed by the Brush Company. This machine is modified from the original Brush

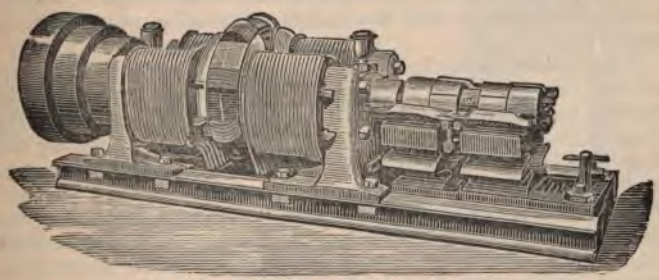

FIG. 28.—THE BRUSH PLATING DYNAMO.

lighting dynamo, and has an armature, which may be described as an open coil disc armature in opposition to the closed coil disc of the Victoria dynamo.

To explain the action of a dynamo machine more fully, we will suppose NS, NS (Fig. 29), to represent the poles of compound horse-

shoe magnets, which are towards the observer. A is the axle, and B, C, D, and E are the ends of four horizontal insulated armature coils, moving in the direction of the large arrows. When a coil of insulated wire is moving *towards* a pole of a magnet, a current of electricity is developed in the wire in *one* direction, and when the coil is moving *from* the pole of the magnet, a current is produced in an *opposite* direction. These currents are reversed in direction if the pole of the magnet is reversed; so that the current developed in a wire by moving it *towards* the *south* pole of a magnet, is the same in direction as that produced by moving it *from* the *south* pole. We will now suppose that the current produced in the wire B, moving from S to N, is in the direction of the small arrow surrounding it, viz., *left*-handed motion; if so, the current of the wire D will also be *left*-handed in direction, because it also is moving from a south to a north pole; whilst the currents in the wires C and E will be *right*-handed, because both those coils are moving from north to south poles.

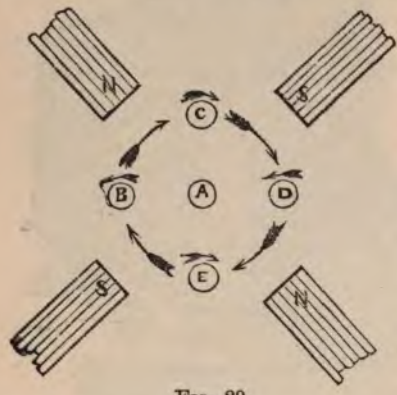

FIG. 29.

From these remarks, by careful attention, it may be perceived:—1st, that the currents of electricity, in all the coils, are reversed in direction four times in every revolution; 2nd, that to obtain a current of one uniform direction from all the four coils (by conducting the whole four into one stream), during *only one quarter* of a revolution, *i.e.*, from one pole to the next one, it is necessary to connect the ends of the wires of the coils of B and D of in an opposite manner with the bars of the commutator (Fig. 23), to those of the coils of C and E; and, 3rd, that as the currents in all the coils are reversed in direction, the two springs which press upon the semi-cylinders, must, by some means or other, be reversed in their order of connection with all the wires every time, and at the same moment, that the reversal of direction takes place in the coils, in order to throw the whole of the currents during a complete revolution into one uniform direction in the springs and in the wires which convey the currents from the terminals of the machine to the depositing vessel.

70. The Voltaic Battery.—Each of the arrangements of metals and liquids which have been described under the head of "Facts," and which develop a current of electricity, constitutes an elementary voltaic battery—a battery in all its essential parts, but not in outward form. All voltaic batteries consist of one or other of those theoretical arrangements modified and adapted for practical use, and are composed either of two metals and one liquid, or two metals and two liquids, because these two arrangements develop the greatest amount of electricity, and are most convenient in use. In the theoretical form, any kind of metal of any size or shape, with almost any electrolytic liquid, and with any kind, shape, or size of containing vessel, will develop a current of electricity and produce deposition; but a practical battery consists of particular metals and liquids, of particular sizes, shapes, and proportions, and at certain distances apart, with suitable screws attached for connections, and with containing vessels made of particular materials, and of special forms and sizes.

71. The kinds of batteries most in use for electro-deposition are—

1st. The old zinc and copper battery (Fig. 30), each pair of which consists of a cross piece of wood (B) at the top, with a groove in it for passing down the zinc plate, and two copper plates (D), one on each side of the zinc, which are prevented from touching it by a slight frame of wood attached to the cross piece; the zinc plate is movable vertically, and has a strong cramp binding screw (Fig. 31) attached to support it at any given height, and with which to form connections; the copper plates are connected together by a strip of sheet copper, by means of a cramp binding screw; they do not touch the bottom of the vessel by several inches, being supported by the cross head upon the upper edges of the vessel.

Fig. 31.

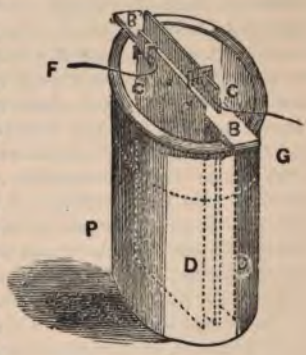

Fig. 30.

2nd. Smee's battery of zinc and platinized silver is similar in arrangement to the one described, except that the sheets of platinized silver being exceedingly thin, are stuck upon the board by shellac varnish, the board being previously saturated with that substance to prevent the battery liquid from acting upon it.

3rd. Daniell's battery (Fig. 32), consisting of a piece of zinc, either in the form of a round bolt or thin cylinder; this is immersed in dilute sulphuric acid, and a cylinder of sheet copper immersed in a solution of sulphate of copper, the two liquids being separated by a porous diaphragm; the zinc is generally contained with the dilute acid in a porous vessel, which is immersed in an outer vessel combining the cylinder of sheet copper and the sulphate solution, or the outer vessel itself is formed of copper, and constitutes the negative metal. In each case a small perforated shelf is placed near the upper end of the battery, containing crystals of sulphate of copper for supplying the outer liquid.

FIG. 32.

4th. For purposes where a current of considerable electromotive force (E.M.F.) is required, a battery consisting of carbon and zinc, in a solution of chromic acid, is sometimes provided.

72. **Battery Cells.**—The form of cells for these batteries is generally either round or square; for *small* batteries, either of the old zinc and copper kind, or of Smee's arrangement, square ones are generally used, but for small Daniell's batteries, or for large batteries of either of these kinds, round vessels are almost invariably adopted. They are made of stoneware, glass, or gutta-percha. The first of these is universally used for large batteries of all kinds; glass is too expensive for large vessels, but it possesses the great advantage of enabling the operator to watch the action of the batteries, and is now being moulded into large vessels for the use of some of the electro-plate manufacturers; gutta-percha has also been used, but possesses rather less advantage upon the whole than the other materials, being opaque and expensive, while the zinc salt of the battery liquid passes rather rapidly over its edges by capillary action.

73. **Porous Cells.**—When Daniell's or any other battery with two liquids is used, porous vessels are required to allow the two liquids to touch each other without mixing; they are of three kinds—unglazed earthenware, wood, and bladder. The first of these is the only kind in use by manufacturers; they should always be kept in clean water when not in use, to remove the salts of the battery liquids from them, to prevent their cracking, and to preserve them ready for immediate use.

74. **Zinc for Batteries.**—The best kind of zinc for batteries, and the kind chiefly in use by electro-platers, is the German or Liège zinc,

known as "Mosselman's," from the name of a former manufacturer of it. The thickness of the plate should vary with the size of the battery; the smallest should not be less than one-eighth of an inch thick, on account of its brittleness when amalgamated; large ones are generally about one quarter or three-eighths of an inch in thickness. Zinc bolts for Daniell's batteries are generally made by melting together a number of old worn-out pieces of battery plates, and casting it in a suitable mould. Silesian zinc is also much used.

75. **Amalgamation of Zinc.**—Zinc plates or bolts are best amalgamated by immersing them about five or ten minutes in a mixture of about one part of sulphuric acid and ten or twenty parts of water; then pouring mercury upon them, and rubbing it all over them with a hare's foot or piece of old cloth, using a small hard brush for the refractory places; they are then washed in water, and drained for half an hour, and brushed, to recover the superflous mercury. All grease must be first removed.

76. **Copper and Platinized Silver for Batteries.**—Ordinary sheet copper may be used for this purpose, and platinized silver may be obtained of most philosophical instrument makers, or it may be easily prepared by any one of the following means:—Immerse a piece of zinc in dilute sulphuric acid contained in a porous cell, place the cell in an outer vessel, and fill the outer space with water, to which a few drops of sulphuric acid have been added; add to this a sufficient quantity of a solution of bichloride of platinum to render it of a brown colour; immerse the piece of silver to be platinized in the outer liquid, and connect it by a wire with the piece of zinc; gas will soon be evolved from the surface of the silver, and the silver will gradually become black with a deposit of platinum; it may then be removed, dipped several times in water, and afterwards dried, care being taken not to rub off the platinum. The porous cell requires to be immersed a short time beforehand. The solution of bichloride of platinum may be easily and quickly formed by adding scraps of platinum foil to a hot mixture of one measure of nitric acid and two and a-half measures of hydrochloric acid, as long as gas is evolved from them; the liquid will then be of a deep red colour.

Silver alone is not nearly so effective for the negative metal of voltaic batteries as platinized silver, because the hydrogen gas evolved adheres very strongly to it, and greatly reduces the amount of its surface in contact with the liquid. The platinum being a very negative metal, and being deposited in the state of a fine powder, causes the hydrogen to be thrown off very rapidly from its surface, and thus increases the action.

Copper plates are less effective than silver, because the battery liquor corrodes them and forms a salt of copper, which dissolves in the liquid

and re-acts upon the zinc, causing it to waste rapidly; for this reason they cannot, like silver ones, be safely left in the liquid any great length of time when the battery is not at work. In addition to this, when they are taken out and exposed to the air they soon become covered with a film of oxide, which considerably weakens the electric current on their re-immersion.

77. **Depositing Vessels, Vats, &c.**—The depositing vessels are made of various materials. For small operations nothing is so suitable as glass vessels or a stoneware pan; but for ordinary manufacturing purposes, vats containing from twenty to several thousand gallons are used; they are generally made of wood lined with sheet lead; but very large ones, for containing sulphate of copper solution, such as are used

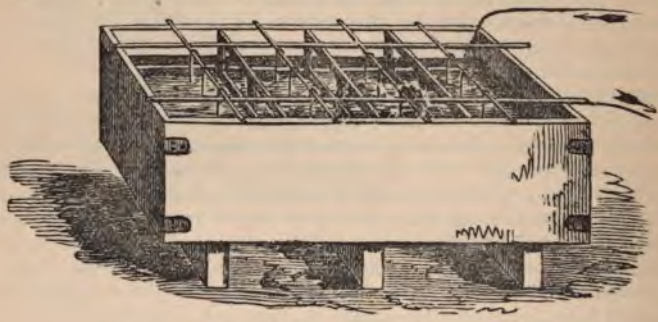

FIG. 33.

for depositing life-sized figures in copper, have in some instances been built of bricks, coated with cement, and lined with gutta-percha. Vats used to contain cyanide solutions should not be lined with this substance, because the cyanide of potassium acts upon it. The vats used for ordinary silver plating are about twenty-four or thirty inches deep, from two to three feet wide, and from three to twenty feet long; their dimensions vary greatly in different manufactories, and depend upon the number and size of the articles to be plated in them. Some electro-depositors use vats formed of sheets of wrought iron riveted together; but there is always a slight salt or sediment found on their sides, which settles at the bottom of the liquid; the anodes should not touch these vessels.

78. **Arrangements of Dissolving Plates in Vat.**—In the vats used for silvering common articles, such as spoons, knives, forks, teapots, plates, &c., the dissolving plates are sometimes fixed all round the sides of the vessel just beneath the surface of the liquid; in addition to this,

vertical wooden frames are fixed at intervals of about two feet, across the vat (Fig. 33), with dissolving plates upon them, and all those plates are connected together metallically. The articles to be plated are suspended by small copper wires, from brass or copper tubes resting across the vessel upon two other and longer tubes passing along the upper edges of the vat. These latter are connected by a large copper wire with the negative pole of the battery, whilst the dissolving plates are connected by another large copper wire with the positive pole; by this arrangement each row of articles has dissolving plates all round it, which greatly facilitates the rapidity of deposition. The wooden cross frames are movable, so that when large articles are to be plated, one or more of them may be removed to make room. Anodes of silver, copper or brass, in cyanide solutions, are usually suspended by stout wrought-iron wire hooks, or better by thick bands or wires of the anode metal, the wires being protected from corrosion at the surface of the liquid by being enclosed within glass tubes; iron does not require protection.

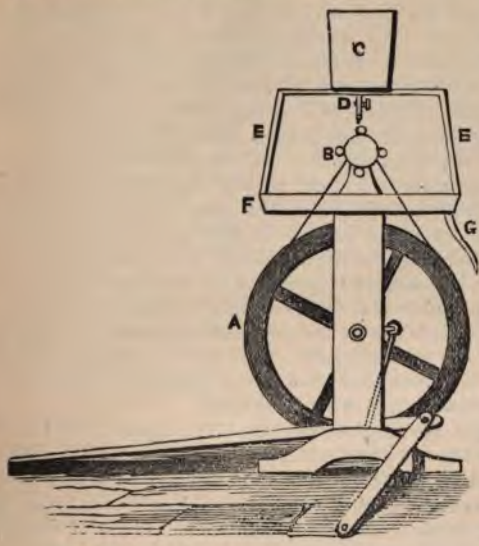

FIG. 34.—"SCRATCH-BRUSH" LATHE.

79. The large vessels used for depositing solutions which require to be worked *hot*, such as the cyanide coppering or brassing liquids, are formed either of cast iron, wrought iron, or iron coated with enamel; and the smaller vessels, such as are used for gilding, are oftentimes of stoneware or glass; enamelled iron pans are also used for this purpose.

80. **The "Scratch-brush" Lathe.**—The depositor will require several "scratch-brush" lathes, one in each depositing room, for scouring and preparing the surfaces of metal articles to receive a deposit. This instrument (Fig. 34) consists simply of an ordinary lathe A, with a

wooden chuck B, to the sides of which are firmly secured four horizontal bundles of fine brass wire; above it is a vessel, C, containing stale beer, which is allowed to drop constantly, by the pipe and tap D, upon the revolving brushes whilst working; the sides E E are to prevent splashing, and the tray F and pipe G are to collect and remove the waste liquid. The workman stands opposite the end of the machine in using it, working the treadle with his foot, and pressing the article against the ends of the revolving wire brushes, exposing in succession different parts of the article to their action. Wire of different degrees of fineness is used with different articles.

81. **Connecting Wires.**—The depositor should provide a large number (several pounds weight) of pieces of copper wire, of about the size No. 18 or 20 of the Birmingham brass wire gauge, and about fifteen or twenty inches long, for suspending the smaller and more numerous articles to be coated in the depositing solutions; a few other pieces of a larger and stronger kind should be provided for the heavier articles. Copper is the most suitable metal for connecting-wires, and the most generally used, because it is one of the best conductors of electricity, being also flexible and not expensive; next to it we should select brass; silver is the best conductor, but is too expensive. Each wire is protected from corrosion by a short glass tube.

82. **Dipping Liquids, Pickling Liquids, &c.**—The depositor will next prepare his various liquids for cleansing articles for plating. For cleaning iron articles he will require large stoneware pans and jars, containing a mixture of one part of sulphuric acid, and twenty parts of water; a weaker solution may be used for some kinds of metal; smooth wrought iron requires a weaker liquid than rough cast iron. For cleaning either copper, brass, or german silver, he will require several stoneware pans, one containing strong nitric acid, another filled with "dipping" liquid (a mixture of 64 parts of water, 64 parts sulphuric acid, 32 parts nitric acid, and 1 part of hydrochloric acid), and a third containing "spent" liquid, *i.e.*, either nitric acid or dipping liquid the power of which has been partly exhausted. In addition to these liquids, he will require some glass-cutters' fine sand; with several small hand-brushes and pieces of old cloth, for brushing and rubbing the sand upon the more rusty and refractory parts of the metal to be cleaned; also a file and scraper to further assist in cleaning them. Hydrofluoric acid, contained in a small leaden or gutta-percha bottle, should be at hand, to apply to the "glazed" patches occasionally met with upon cast iron.

83. **Battery Liquids.**—The usual kind of acid used by electro-platers to excite their batteries is sulphuric acid; it is obtained in large quantities at about a penny or three-halfpence per pound. For the negative solution of Daniell's batteries, a stock of sulphate of copper

should be provided; its price is about fivepence per pound. For Bunsen's battery, bichromate of potash is required.

84. **Liquids for Causing Adhesive Deposits.**—Solutions of nitrate, or of cyanide of mercury, will be needed for preparing the surfaces of copper, brass, and german silver, for receiving adhesive deposits of silver. The nitrate solution is prepared by adding one ounce of mercury to sufficient nitric acid, diluted with three times its bulk of distilled water to dissolve it; no more mercury must be added than the liquid will dissolve; when thoroughly dissolved, dilute it with about one gallon of water. To prepare the cyanide solution, dissolve one ounce of mercury as stated, dilute it with water, and add a solution of cyanide of potassium to it, just as long as a precipitate is produced; filter it, add a small quantity of water to the precipitate in the filter, and, when completely drained, take out the precipitate and add to it a strong solution of cyanide of potassium until it is all dissolved, then add a little more cyanide solution, and finally dilute it with water until the whole measures one gallon. The solution when prepared is kept in a large stoneware pan, a pan of dipping liquid and another of water being near it, and each placed near the scratch-brush lathe and depositing vats in the silvering-room.

85. **Materials for Moulding.**—The electro-depositor who includes in his business not only the ordinary electro-plating, but also the manufacture of works of art by deposition, requires a number of substances for moulding and preparing the surface of the moulds to receive a deposit. For moulding ordinary metal objects, he often uses gutta-percha or a composition consisting of equal parts of white wax and spermaceti; but one of the best substances we have used for this purpose has been a composition, consisting of two parts of gutta-percha and one part of Jeffery's marine glue; the glue is cut up into small pieces and melted at a gentle heat in an iron ladle, the gutta-percha, also cut very small, is then added, and the mixture constantly and vigorously stirred at a gentle heat until the two are thoroughly incorporated. This substance possesses several important advantages over gutta-percha alone as a moulding material; it is softer when heated, and takes a sharper impression; it contracts more in cooling, and is therefore more easily removed from the original; and in taking the blacklead it is very superior to gutta-percha. With ordinary care many copies may be taken by deposition off one of these moulds; we have taken a dozen from one of them.

86. **Elastic Moulding Composition.**—When the objects to be copied are much under-cut, or when we wish to take a mould of a bust all in one piece, elastic moulding composition is required. The best substance of this kind, and almost the only one used, is composed of four parts of best Russian glue and one part of treacle; the glue is broken

into small pieces and soaked for one or two hours, or until it is quite soft, in sufficient *cold* water to cover it; when it is soft the superfluous water is thrown away, and the glue, together with the treacle, is heated in a common glue-pot, like ordinary glue, and stirred until the two substances are thoroughly mixed; the use of the treacle is to prevent the mould drying and shrinking. Some under-cut objects are copied in warm gutta-percha under hydraulic pressure.

87. **Blacklead, Phosphorus, Liquid, &c.**—For rendering the surfaces of non-conducting substances, such as gutta-percha, wax, marine glue, &c., conductible, the following substances are used:—

1st. The common powder blacklead for ordinary non-elastic moulds; there is a great difference, however, between different specimens of blacklead in their value for this purpose, some causing the deposit to spread over the moulds very quickly, whilst others scarcely cause it to spread at all; the best we have found, and it has been very good, is "Dix's," sold in twopenny packets, one or two of which will serve the operator a long time for this purpose with small articles.

2nd. For moulds of elastic composition (§ 86) the depositor will require the following liquids, patented by Mr. Alexander Parkes:—A, the phosphorus solution—to make nearly three ounces of which, melt 64 grains of bees-wax or tallow; then dissolve eight grains of india-rubber cut up very small, in 160 grains of bisulphide of carbon, and when it is dissolved add to it very carefully (as it is highly inflammable) the melted wax, and stir the mixture thoroughly; then dissolve 64 grains of phosphorus in 960 grains (about 2¼ ounces) of bisulphide of carbon, and add to it 80 grains of spirit of turpentine, and 64 grains of asphalte in fine powder; when dissolved, add this solution to the previous one of india-rubber and wax, and thoroughly mix them by stirring. B, the silver solution—to make twenty ounces (one pint) of this liquid, dissolve about 18 or 19 grains of pure silver in about 20 or 25 grains of the strongest nitric acid, and then dilute it to the required volume with *distilled* water. And C, the gold solution—to make 20 ounces of which, dissolve about five or six grains of pure gold in about 20 or 25 grains of a hot mixture of one measure of nitric acid, and about two or three measures of hydrochloric acid, and, when dissolved, dilute the solution with 20 ounces of *distilled* water.

The same inventor includes in his patent a phosphorus moulding composition, by the use of which the immersion in the phosphorus solution is dispensed with, the moulds themselves containing the required amount of phosphorus; to make about one pound of this composition, melt together half a pound each of wax and deers' fat, then dissolve about 19 or 20 grains of phosphorus in about 300 grains of bisulphide of carbon; keep the wax mixture barely melted, and add the phosphorus solution slowly to it, and with brisk stirring of the fat,

pouring it in at the bottom of the melted mixture by a vessel with a long spout to prevent its inflaming. It is highly dangerous to leave spilt portions of the phosphorus composition where it can come in contact with wood, paper, rags, &c., as after a lapse of some time (even hours) they will often burst into flame.

88. **Selection of Depositing Processes.**—For very small articles of which there are a great number, such as buttons, hooks and eyes, pins, &c., and which require only a very thin deposit, the simple immersion or wash process will answer very well, being both easy of execution and cheap. For the multiplication of numerous small articles in copper, such as medallions, &c., the single cell process is very advantageous; it is quicker than the battery one, and considering the time occupied, and the other elements of expense, it is to be preferred to that method. But for all ordinary deposits, plating, &c., the battery process is by far the best, because coatings of any thickness, in all ordinary metals, may be obtained by it, and the solutions do not, as in the other processes, require renewal.

89. **Methods of Making Depositing Solutions.**—The operator will next consider about making depositing liquids. They may be made by two methods, the one called the chemical and the other the battery process. The chemical one consists in mixing the various ingredients by the usual chemical means, and in suitable proportions to form the complete liquid; for instance—1st the ordinary sulphate of copper solution is prepared by dissolving a certain proportion of commercial sulphate of copper in water, and adding to it a certain proportion of sulphuric acid to form *free* acid; and, 2nd, to form the ordinary cyanide of silver and potassium plating liquid, silver is dissolved in dilute nitric acid; the solution of nitrate of silver formed is precipitated by addition of a solution of cyanide of potassium; the white precipitate of cyanide of silver is washed, and then added, as much of it as will dissolve, to a solution of cyanide of potassium; after that an additional portion of cyanide of potassium is added to form *free* cyanide. The battery process consists in taking some water and dissolving in it a certain proportion of acid or salt, as the case may be, then placing a large anode of the given metal at the lower part of the liquid, and a small bright cathode at the upper part, and, if necessary, applying heat, and connecting them with a suitable battery until the required quantity of metal is dissolved, which is indicated by the cathode receiving a good deposit. In making gold solutions the cathode is generally placed in a small porous cell filled with the same liquid, and immersed nearly to its edge in the outer liquid, and by transferring the cathode occasionally to the gold solution, and observing if it receives a good deposit, we may know that sufficient metal is dissolved; the liquid of the cell may then be added to the outer solution. If it is wished to make

sulphate of copper solution by this method (which is not advisable, however, the salt being so cheap), take the same quantity of water as is necessary for the chemical method, and add to it as much acid as was contained in the salt of copper, with the free acid as before, and then pass a current from a battery of one or two pairs by a large anode and small cathode, until sufficient metal is dissolved; or, if it is desired to make some cyanide of silver and potassium solution by this method, which is sometimes done, take the same proportions of water, cyanide of potassium, and free cyanide as in the chemical process, and pass the electric current by a large silver anode, until the same proportion of silver is dissolved as is required in the chemical method.

90. **Selection of Depositing Liquids.**—The following rules should be observed in selecting a suitable depositing liquid for the battery process:—

1st. It should act strongly upon the anode, and hold abundance of metal in solution.

2nd. It should possess good electrical conducting power.

3rd. It should yield its metal freely, and in a reguline state.

4th. It should not act chemically to any great extent upon any base metals, because it is those we generally wish to coat, and chemical action upon them would endanger the adhesion of the deposited metal.

5th. It should not decompose by contact with the atmosphere, nor should light influence it in such a way as to injure it for depositing purposes.

6th. It is better if it does not evolve gas at the surface of the receiving article whilst depositing, because that generally indicates a waste of battery power attended by oxidation of the liquid.

91. **Testing a Depositing Liquid.**—To test a depositing liquid, pass a current of electricity through it, from about two pairs of Smee's batteries, with a suitable clean anode of proper size, and a clean piece of iron, brass, or copper, of about the same size, to receive a deposit, observing how much gas is evolved in the battery. If the deposit appears quickly, and is of a bright and proper colour, and if it adheres to the metal; if the cathode evolves gas from its surface, and the anode dissolves freely, cleanly, and without an escape of gas, work it at intervals, keeping it exposed to light and air; observe if it continues to work well, or whether, on the contrary, it shows a decrease of conductibility, deposits a sediment, or if the anode becomes covered with an insoluble crust (this last may arise either from deficiency of free acid or from impurities in the metal). If but little gas is evolved in the battery, it is a bad conductor, and will neither dissolve nor deposit the metal freely at that temperature, or it is deficient in *free* acid or *free* salt. If the deposited metal is of a bad colour, either the battery is too strong, the receiving article too small, or the liquid is incapable of yielding good

metal. If the immersed metal or article is coated by simple immersion without the aid of the battery, it shows that, to adapt the liquid to articles made of that particular metal or alloy, they must receive some previous preparation, in order to make the deposit adhere. If it deposits a sediment, or alters in conductibility by exposure to the air and light, the greater probability is that those influences alter either its chemical composition or the arrangement of its particles. If it evolves gas at the receiving surface during deposition, it shows either that there is too much battery power, too little metal in solution, too much *free* acid, or that it is a wasteful liquid, in which one part only of the current is employed in depositing metal, whilst another part of it is employed in depositing gas and oxidising the liquid.

92. **Testing Solutions for Depositing Alloys.**—With solutions in which alloys are to be deposited the most important condition is that neither of the metals to be deposited are electro-positive to each other in that liquid. This is best tested by taking a wire of each metal, connecting them with a galvanometer, and simultaneously immersing their free ends in the liquid; if either is electro-positive, the needles of the instrument will be deflected, and the direction of the deflection will indicate which is positive, while the amount of deflection will indicate the amount of their electric difference in that liquid. It may also be tested by immersing a wire of each metal (not in mutual contact) in the liquid; if either becomes coated with metal in an hour, that one is positive; but if neither becomes coated in six hours, there is no perceptible electric difference between them.

93. The following experiments bear upon this part of the subject, and show that if a liquid contains two metals in solution, and a wire or other piece of each of those metals is immersed in the liquid, and one becomes covered with a deposit of metal, while the other does not, the one so covered is electro-positive to the other in that liquid, and the solution will only readily yield the same metal which is deposited by simple immersion:—

1st Experiment. With an alloy solution consisting of equal measures of a strong solution of protochloride of tin and terchloride of antimony, with an anode either of tin or antimony (the latter is the most proper, because it does not coat itself by simple immersion in the liquid), a copper cathode, and one pair of small Smee's batteries, only antimony was deposited; tin coated itself with antimony in this solution by simple immersion, and was found by the galvanometer to be strongly positive to that metal.

2nd Experiment. With a liquid composed of equal measures of a solution of protochloride of tin and chloride of bismuth, and either a bismuth or tin anode (the former is better), a brass cathode, and one pair of small Smee's batteries, only bismuth was deposited; tin was

positive to bismuth in this liquid by the galvanometer, and coated itself quickly with that metal by simple immersion.

3rd Experiment. With a mixture of equal measures of terchloride of antimony and chloride of bismuth, antimony anode, copper cathode, and a feeble Smee's battery, only antimony was deposited; bismuth coated itself slowly with antimony by simple immersion, and was found by the galvanometer to be moderately positive to the latter metal in the solution.

4th Experiment. With 100 grains each of protochloride of tin and chloride of zinc dissolved together in an ounce of distilled water, tin anode, copper cathode, and one pair of small Smee's batteries, only tin was deposited; zinc was positive to tin in this liquid by the galvanometer, and deposited tin upon itself by simple immersion.

5th Experiment. With equal measures of strong solutions of nitrate of zinc, and ternitrate of bismuth, and a little nitric acid, bismuth anode, copper cathode, and a feeble one-pair battery, only bismuth was deposited; zinc was strongly positive to bismuth in this liquid by the galvanometer, and coated itself quickly with that metal by simple immersion.

6th Experiment. With a solution of the mixed sulphates of zinc and copper, copper anode and cathode, and a single small battery, copper alone was deposited; zinc was strongly positive to copper in this liquid by the galvanometer, and coated itself immediately with copper in it by simple immersion.

94. Further, if we take some distilled water, and caustic potash is dissolved in it, passing a moderately strong current through it by platinum electrodes, hydrogen gas will alone be set free at the cathode; in this case also, hydrogen—the least positive of the two positive elements of the liquid—potassium and hydrogen—is set free or deposited. If we now add enough sulphuric acid to the liquid to convert it into a solution of sulphate of potash, add some sulphate of zinc beside, and pass a weak current through, we shall obtain a deposit of zinc on the cathode, but no hydrogen or potassium. In this case we cannot determine by the galvanometer which is the most positive in this liquid, hydrogen or zinc, because the former is a gas; but it is probable that hydrogen is the most positive, because zinc does not evolve it by simple immersion in this liquid. If we further add to the liquid a small quantity of sulphate of copper, and treat it as before, neither potassium, hydrogen, nor zinc will be deposited, but only copper; and we find by the galvanometer that copper is less positive than zinc in such a liquid, and that zinc coats itself with copper in it by simple immersion; in this case also the least positive of the positive elements of the liquid is alone deposited. From these and many other experiments, which we *have tried with* similar results, we deduce the following rule:—If a

liquid contains several metals or other electro-positive substances dissolved, and a *weak* electric current is passed through it, only that substance which is the least electro-positive is deposited.

95. With regard to the influence exercised by the proportions of the ingredients of the liquid and the strength of the current, we may observe, that, if a liquid contains several metals dissolved in equal quantities, and only one is being deposited by the passage of a weak current, a considerable increase in the strength of the current will cause a portion of the next more positive metal to be deposited along with the less positive one; but this alloy deposit will not be very coherent, because the power required to deposit the second metal in the reguline state will be so great as to deposit the first as a soft powder. This holds most true when the difference of electric power required is great; for instance—1st. If small and equal quantities of sulphate of zinc and sulphate of copper are dissolved together in a large quantity of water, and a feeble current passed through the solution, only reguline copper will be deposited; but if the battery power be considerably increased, either by a greater number or larger surface of the battery plates, the deposit of copper will cease to be reguline, and zinc will be deposited with it. If the power be still further increased, hydrogen gas will also be evolved at the surface of the deposited metals. 2nd. If we dissolve a small quantity of sulphate of copper, and a large quantity of sulphate of zinc, in a large quantity of water, and pass a strong current through the solution, copper, zinc, and hydrogen will be set free at the cathode. 3rd. If we slightly moisten a lump of caustic potash with pure water, and pass a weak electric current through it by platinum electrodes, hydrogen alone will be set free at the cathode, but if a very powerful current is employed, potassium also will be deposited. In each of these cases we find that when the current is weak the least positive of the positive substances is alone deposited; but if the power is sufficiently increased, and there is only a small proportion of the less positive substance present, the more positive substances, even though they are much more positive, will also be liberated. Thus the weaker affinities are overcome first, and to the greatest extent; the current of electricity exercising its influence first, and in the greatest proportions, upon the salt of the least positive metals.

96. **Depositing Liquids.**—For the benefit of the practical depositor—to whom a general knowledge of all solutions from which ordinary metals may be deposited, with their respective advantages and disadvantages, is of considerable importance—we will give a description of those solutions in regular order, making such remarks in our progress as will be likely to assist him in the selection of those most suitable for his particular purposes.

97. *Antimony Solutions.*—The most common salts of antimony are the sulphide, terchloride, and potassio-tartrate. The hydrochlorate of terchloride of antimony, *i.e.*, the ordinary chloride of antimony, as prepared for pharmaceutical purposes, is formed by chemical means thus:—Take one pound of black sulphide of antimony, add to it four pints of hydrochloric acid, gently heat the mixture with constant stirring, until the gas evolved decreases, then boil it slowly down to two pints, keeping it partly covered all the time; cool it, filter it through calico, and keep it in a stoppered bottle. It is now a yellowish red liquid, of specific gravity 1·47, but becomes nearly colourless by depositing antimony from it by the battery process. The commercial article contains much dissolved iron.

A similar solution may be made by the battery method; this consists in passing a current from several pairs of batteries through strong hydrochloric acid by a large anode of antimony, until a good deposit is obtained; this liquid is nearly free from iron. The chloride of antimony is an excellent conductor of electricity, it dissolves the anode freely, yields plenty of bright reguline metal if the battery power is sufficiently weak, and its depositing power does not deteriorate by exposure to light or the atmosphere; it appears not to be gradually exhausted by working; it is decomposed more or less rapidly by zinc, tin, lead, iron, brass, copper, and german silver, each of which coats itself in it with antimony by simple immersion, and articles immersed in it require to be washed with hydrochloric acid before washing them with water, otherwise the latter decomposes the adhering liquid and covers them with a white insoluble powder.

98. The mixed chlorides of antimony and ammonia form a very good depositing liquid. It may be formed either by the battery process, by mixing one measure of a saturated solution of sal-ammoniac with one measure of hydrochloric acid, and working antimony into it by means of a current and a large antimony anode; or by simply mixing together equal measures of a saturated solution of sal-ammoniac and commercial chloride of antimony. This solution conducts easily, yields its metal freely and of good quality, and does not act so strongly upon base metals as chloride of antimony alone; but in other respects it is similar to the chloride. The mixed chlorides of antimony and manganese, or of antimony and bismuth, yield a reguline deposit easily, but do not appear to possess any special advantages.

99. The potassio-tartrate of antimony is a salt not very soluble in water; its aqueous solution is a very bad conductor of electricity, and is not to be compared to the chloride for depositing purposes. We have never been able, either with strong or weak batteries, to deposit from it anything better than a small quantity of antimony in the

state of a perfectly black powder; on the other hand, its solution in hydrochloric acid (which dissolves it very freely), or hydrochloric acid and water, is by far the best solution for depositing antimony that we have tried. It is a most excellent conductor of electricity; it is not impaired by long working or exposure to light or the atmosphere (we have deposited antimony from it constantly during many months); it will bear a very great amount of battery power without the deposit passing into the state of a loose powder; it deposits reguline metal very rapidly and in great thickness. We have obtained such deposits from it upwards of two inches in thickness; articles immersed in it wash clean in water alone without the previous use of hydrochloric acid; it may be made by mixing together about two pounds of water, four pounds of hydrochloric acid, and eight pounds of potassio-tartrate of antimony; a greater proportion of water may be used if desired.

100. Both the black and red sulphides of antimony dissolve in cold hydro-sulphate of ammonia, and the resulting solutions conduct very freely with an antimony anode and one pair of Smee's batteries, but yield no deposit of metal even with a battery of twenty-five pairs in series. Aqueous solutions, either of caustic potash, tartrate of potash, or oxalate of potash, scarcely conduct at all with an anode of antimony, and a battery consisting of one or two pairs. Cyanide of antimony dissolved in a solution of cyanide of potassium has been proposed as a depositing liquid, but we have found a solution of cyanide of potassium to be a very bad conductor with an anode of antimony.

101. Antimony is one of the easiest metals to deposit in the reguline state; its appearance when deposited from the chloride solutions, and from the solution of the potassio-tartrate in hydrochloric acid, is very beautiful, and when deposited slowly it has much the appearance of highly-polished steel. Some of its properties when thus deposited are very peculiar and interesting, especially with regard to heat:—If, during any part of the time the deposit is progressing, the deposited antimony be taken out and struck gently or rubbed with any hard substance, such as metal or glass, an explosion occurs, accompanied with a small cloud of white vapour, and rather strong acid odour, and nearly always with considerable heat, sufficient to burn one's fingers, melt gutta-percha, burn paper, and even scorch deal wood quite brown, especially if the deposit is thick; and invariably accompanied by fracture of the deposited metal; sometimes, if the process of deposition has been interrupted and the deposited metal is not homogeneous, a fracture is extended quite through the metal to upwards of one-eighth of an inch in depth. This phenomenon has been observed many times both before and since its first publication; in several instances the explosion took place even in the

liquid, by striking the deposit against the glass containing vessel; and in one instance it occurred spontaneously after the metal had been washed with dilute hydrochloric acid, dried, and had remained out of the liquid several hours.

On one occasion, a deposit had been well washed, dried, and out of the solution many hours, and a friend, in course of conversation, was unconsciously breaking small portions off it with his fingers, when it became suddenly heated and exploded, causing a slight noise like the lighting of a congreve match, and burning his fingers. On other occasions a deposit has been progressing, and has been removed an instant for examination, and the battery liquid strengthened by the addition of acid; upon examining the deposit a few hours afterwards, it has been found cracked in various directions, as if an explosion had occurred in the interval, although the apparatus had been undisturbed.

A French writer has suggested that this deposit is a compound of antimony and hydrogen; and from the fact that the explosions occurred when the metal was depositing rather rapidly, we are inclined to think his explanation correct; the extra power, as we have seen in other cases (§ 94, § 95), causing hydrogen deposit, which, in its nascent state, instead of being evolved, might combine with the metal and form an explosive compound. Another suggestion we would make is, that the metal is deposited in a peculiar condition of unequal mechanical tension, similar to that of unannealed glass, and that, by breaking, the closer aggregation of the particles may develop light and heat. (Phil. Trans. Roy. Socy., 1857, 1858, 1862.)

Since the foregoing was written, "explosive" deposited antimony has been analysed by the author of this book, and the temperature acquired and amount of heat evolved by its explosion determined. The freshly deposited active metal contains a small percentage of chloride of antimony; it rises in temperature between 600 and 700 Fahrenheit degrees when exploded, and evolves sufficient heat to melt tin. It very slowly loses its power at atmospheric temperature; a thick bar requires several years to do so completely, but if kept warm it decomposes very much more quickly; in each case it gradually evolves acid matter and loses its brightness.

All electro-deposited metals are in a state of unequal molecular strain. Copper, when electro-deposited upon the bulb of a thermometer, compresses it with considerable force, upwards of 100 pounds per square inch, and causes the mercury to rise in the tube. Cadmium, similarly deposited, slightly expands the bulb, and causes a depression of the mercury. These actions have been termed "electro-strictions." The author has found analogous effects by depositing metals upon pieces of very fine wire whilst in a stretched condition.

102. Another peculiarity in depositing antimony from the potassio-tartrate solution is, that if the solution be a very dense one, and the process long continued without disturbance of the liquid, the deposit occurring upon the cathode will slowly spread out, in the form of a thin sheet upon the surface of the liquid, until it touches the anode; whilst the coating beneath progresses very slowly. We have a button of antimony formed in this way upon a vertical copper wire, one and five-eighths inches in diameter, the deposit beneath the surface of the liquid having been only half-an-inch thick; it occupied about eighteen days with a small one pair Smee's battery in forming. Deposits of antimony formed in the above solution do not spread over blackleaded surfaces of gutta-percha, nor do they adhere with any great degree of firmness to copper, brass, or iron.

103. *Bismuth Salts.*—The most usual compounds of bismuth are the chloride, mononitrate (pearl white), and ternitrate. The chloride is formed by digesting bismuth filings a long time in warm hydrochloric acid. The mononitrate may be formed by dissolving bismuth to saturation in warm dilute nitric acid, and then adding a large quantity, say fifty or a hundred times its volume of water; the precipitate produced, when well washed with water, is the substance required. The ternitrate is formed by dissolving the metal in hot nitric acid, evaporating the solution, and leaving it in a cold place to crystallize. Bismuth may easily be deposited from a solution formed by dissolving either mononitrate or ternitrate of bismuth in dilute nitric acid, but requires an exceedingly feeble current to liberate it in a reguline state; its appearance when so deposited is very beautiful, white with a faint pinkish tint, and with a fine silky lustre; it does not spread over blackleaded surfaces of gutta-percha in this liquid. A bismuth anode does not dissolve readily in a hot solution of cyanide of potassium.

104. *Zinc Salts.*—There are a variety of salts of this metal in ordinary use, the most common of which are the sulphate, chloride, nitrate, and acetate. The sulphate may be formed by dissolving zinc to saturation in a mixture of sulphuric acid and water, filtering and evaporating the liquid, and setting it in a cold place to crystallize. The chloride is made by digesting hydrochloric acid with zinc, filtering, evaporating, until it is quite oily, and cooling. The acetate is made either by dissolving zinc in strong acetic acid to saturation, then evaporating and crystallizing the solution; or, by adding a solution of acetate of lead to a solution of sulphate of zinc as long as it produces a precipitate; then filter, evaporate, and crystallize the liquid.

105. *Zinc Solution.*—The sulphate of zinc solution for depositing may be formed by dissolving two pounds of the salt in a gallon of

water, and filtering the mixture; but the best sulphate depositing solution we have used has been the spent battery liquid taken from a cell of a Smee's battery, in which there had occurred a very good deposit of zinc upon the platinized silver plate; but with this and with other solutions of zinc there is a great tendency to the evolution of hydrogen gas at the cathode during deposition; they require, therefore, to be worked very carefully and with very feeble battery power. Zinc may be readily deposited, either by the single cell or by the battery process, from a neutral solution of the sulphate; but the single cell is less adapted for its deposition than the battery, because the acid, set free by the deposition of the metal, re-acts upon the deposit, and diminishes its amount. The other solutions, such as the chloride, nitrate, acetate, or the various double salts of zinc with ammonia, or potash, do not appear to possess any great advantages over the sulphate.

Amongst other liquids, that of cyanide of zinc dissolved in a solution of cyanide of potassium has been recommended; but it is a bad conductor with a zinc anode, and requires to be used hot to make it conduct at all freely, or to make the anode dissolve. This might easily have been foreseen from a knowledge of the fact that the affinity of cyanogen for all, or nearly all, the base metals is comparatively feeble. We have found by experiment that a solution of cyanide of potassium will dissolve only about one half as much cyanide of zinc as it will of cyanide of copper. Zinc oxide dissolves somewhat freely in a boiling solution of cyanide of potassium. Cyanide of zinc dissolves freely in a solution of sesquicarbonate of ammonia. Ferrocyanide of zinc is but feebly soluble in a boiling solution either of ferrocyanide (yellow prussiate), or of ferricyanide (red prussiate) of potassium, but it is freely soluble in a boiling solution of cyanide of potassium. Zinc deposits spread over blackleaded surfaces by the battery process, in the same manner as with copper.

106. *Cadmium Solution.*—A patent was taken out on March 19, 1849, by Messrs. Russell and Woolrich for the electro-deposition of cadmium, and the following is their description of the process:—"Take cadmium and dissolve it in nitric acid diluted with five or six times its bulk of water, at a temperature of about 80° or 100° Fah., adding the dilute acid by degrees until the metal is all dissolved; to this solution of cadmium a solution of carbonate of soda (made by dissolving one pound of the crystals of washing soda in one gallon of water) is to be added until the cadmium is all precipitated; the precipitate thus obtained is to be washed four or five times with tepid water; next add as much of a solution of cyanide of potassium as will dissolve the precipitate; after which, one-tenth more of the solution of cyanide of potassium to be added, to form *free* cyanide. The strength of this solution may

vary, but the patentees prefer a solution containing six troy ounces of metal to the gallon. The solution is worked at about 100° Fah., with acetate of cadmium as an anode." White reguline cadmium may be easily deposited from aqueous solutions of its chloride, bromide and iodide, and especially from its sulphate.

107. *Tin Salts.*—The most common salts of tin are the peroxide and protochloride; in addition to these there are two others used extensively in Manchester and the cotton printing districts, viz., the bichloride, and the stannate of soda, *i.e.*, oxide of tin combined with caustic soda. Protoxide of tin is formed by dissolving protochloride of tin in water containing a few drops of hydrochloric acid, and then adding liquid ammonia or a solution of carbonate of potash as long as a precipitate can be produced; the precipitated protoxide of tin should be washed and dried. Protochloride of tin is easily made by adding grain tin to strong hydrochloric acid, and keeping it at 150° or 200° F., until gas ceases to be evolved from the metal; the resulting solution should then be evaporated and crystallized. Aqueous bichloride of tin may be made by dissolving tin in aqua regia not containing too much nitric acid; a mixture of nitric acid with sal-ammonic or common salt may likewise be used. Stannate of potash may be formed by fusing together one equivalent (149·5 parts) of freshly precipitated peroxide of tin, and two equivalents either of caustic potash (112·4 parts), or of crystallized carbonate of potash (138· parts).

108. *Tin Solutions.*—M. Roseleur has patented the following liquids for the deposition of tin:—

1st. For simple immersion or wash process, which may be used for small articles generally:—Dissolve 17½ ounces of ammoniacal alum in 22 pounds of boiling water, and, when dissolved, add 1 ounce of protochloride of tin; the articles to be coated should be well cleaned and then immersed in the liquid, and moved about in it until they are sufficiently white.

2nd. For depositing tin upon lead, iron, steel, copper, or brass, by connecting the articles with a piece of zinc and immersing them in the solution:—Dissolve 10½ ounces of bitartrate of potash in 17½ pints of water, then add three-quarters of an ounce of protochloride of tin, and boil it a few minutes; the articles to be coated are immersed in the solution in contact with a piece of zinc of proportionate size.

3rd. For coating zinc, iron, copper, and many other metals by the battery process:—Dissolve 11 ounces of pyrophosphate of potash or soda in 17½ pounds of water, then add 4½ ounces of protochloride of tin, and operate by the current process with an anode of tin. By this method M. Roseleur states that he can tin metals beautifully and to any thickness. Pyrophosphate of soda is easily formed by heating to redness the common diphosphate of soda.

109. A protochloride of tin depositing liquid may easily be formed by dissolving newly-made commercial protochloride in water, and adding a little hydrochloric acid to remove any cloudiness or white precipitate which may be formed; a similar liquid may be made by the battery process, by passing a current through dilute hydrochloric acid by means of a large tin anode, until sufficient metal is dissolved. This or any other chloride of tin liquid is not a good one to obtain reguline metal from; it has a very great tendency to deposit the tin in the form of long crystalline needles, of a fern-like appearance, which often project from the corners and edges of the cathode to a distance of upwards half-an-inch. A solution composed of 11 ounces of water, 1 ounce of hydrochloric acid, and 80 grains of protochloride of tin, admits of this effect being produced in a striking degree; nearly all the compounds of tin, and especially those formed with mineral acids, exhibit this tendency in a greater or less degree when acted upon by electrolysis, rendering the deposition of tin in thick layers of fine white coherent metal a matter of considerable difficulty.

110. The stannate of potash solution is easily formed either by dissolving the crystallized salt in water, or by dissolving freshly precipitated peroxide of tin while still moist, in a boiling solution of caustic potash. It may also be easily formed by the battery process, by passing a strong current of electricity by a large tin anode through a strong and boiling solution of caustic potash, until the immersed cathode receives a free white deposit. This solution, if worked at 150° Fah., yields a good deposit of fine white metal; but it decomposes by exposure to the atmosphere, and soon deposits all its metal as oxide of tin, at the bottom of the vessel. A solution of cyanide of potassium and tin has been proposed as a depositing liquid; but it is a bad conductor with a tin anode, even when hot, and does not dissolve the metal freely.

111. Mr. Joseph Steele coats zinc, iron, steel, copper, and brass with tin, in his patent solution, by the battery process, thus:—Dissolve 60 pounds of common soda, 15 pounds of pearl-ash, 5 pounds of caustic potash, and 2 ounces of cyanide of potassium, in 75 gallons of water, at 75° Fah., and filter the resulting solution; then add 2 ounces of acetate of zinc, and 16 pounds of peroxide of tin; stir the resulting solution until all is dissolved; it is then ready for use. Work it by the battery process with an anode of zinc or tin, and with the liquid at 75° Fah.

112. **Electrical Relations of Tin and Iron.**—Tin is feebly negative to iron at all temperatures between 62° and 203° Fah. in distilled water, and positive to it at 212° Fah. It is positive to iron at all temperatures between 62° and 212° Fah. in a saturated solution of boracic acid; also the same between those temperatures in a strong solution of phosphoric acid in distilled water; or in 1 measure

of oil of vitriol mixed with either 9 or 96 measures of distilled water; or in a mixture of 1 measure of this acid and 192 measures of distilled water, from 73° to 158° Fah., and negative to iron above that to 212° Fah.; it is positive to iron from 72° to 212° Fah. in a mixture of equal measures of hydrochloric acid and water; it is negative to iron from 70° to 77° Fah., and positive above that to 212° Fah. in a mixture of 1 measure of hydrochloric acid and 9 measures of distilled water; it is negative to iron from 70° to 212° Fah. in a mixture of 1 measure of hydrochloric acid, and 90 measures of distilled water, and positive to iron from 68° to 212° Fah. in 1 measure of hydrofluoric acid and 9 measures of water; it is positive to iron in 1 measure of nitric acid and 9 measures of water from 70° to 111° Fah., and negative from 111° to 212° Fah.; and it is positive to iron from 82° to 212° Fah. in a mixture of 1 measure of nitric acid and 96 measures of water.

113. *Lead Salts.*—The most common salts of lead are the nitrate and the acetate. The nitrate is formed by dissolving lead in dilute nitric acid, taking care that no more lead is added than the acid will dissolve; the resulting solution must be filtered, evaporated, and crystallized; it is a hard, white salt, soluble in water. Acetate of lead is made by digesting oxide of lead in vinegar or acetic acid; filtering, evaporating, and crystallizing the liquid; it is soluble in water. It is called "sugar of lead."

114. *Lead Solution.*—Lead may be deposited from an aqueous solution, either of its nitrate or acetate, or from a solution of plumbite of potash,—the latter is formed by dissolving litharge in a boiling solution of caustic potash; zinc and tin articles (but not iron ones) decompose this liquid and coat themselves with lead in it by simple immersion. It is difficult to deposit any considerable thickness of reguline metal from either of these liquids.

115. *Salts of Iron.*—Among the salts of iron in most common use are the sulphate, chloride, and bromide; they may be respectively formed by dissolving iron in dilute sulphuric, hydrochloric, or hydrobromic acid, evaporating and crystallizing the solution as much as possible out of contact with the atmosphere.

116. *Iron Solutions.*—Iron may be reduced from a solution of its protosulphate (green copperas), made by dissolving metallic iron in dilute sulphuric acid; or from its protochloride, which is preferable, and which is made by dissolving iron in hydrochloric acid. We have deposited it in the state of reguline white metal, by passing a current of considerable intensity (15 or 20 cells), for one hour, through an anode of iron immersed in a saturated aqueous solution of sal-ammoniac; its appearance when deposited from this liquid is rather white, very similar to freshly broken cast iron. By the same means it may

also be deposited, using a saturated solution, either of carbonate of ammonia, acetate of ammonia, or acetate of potash. We have also obtained good metal from a saturated aqueous solution of a mixture of two parts of protosulphate of iron and one part of sal-ammoniac. We have deposited it from an aqueous solution of ferrate of potash, which may be formed either by igniting peroxide of iron (crocus) very strongly for some minutes with caustic potash and saltpetre; or we may make a very strong solution of caustic potash, immerse in it a large iron or steel anode, and a small copper or platinum cathode, and pass a strong current from 15 or 20 cells of Smee's battery through it until it acquires a deep amethyst or purple colour; by that time the cathode will have obtained a coating of iron, which will be in the state of a dark powder if the power has been too great, or it will have the appearance of white cast-iron, or intermediate between that and the appearance of reguline deposited zinc, if the power has been sufficiently weak. This solution rapidly decomposes by contact with the atmosphere, becoming colourless, and deposits all its metal in the state of peroxide at the bottom of the vessel. Iron may be very easily deposited from green vitriol, thus:—Dissolve a little crystalline sulphate of iron in water, and add a few drops of sulphuric acid to the solution; one pair of Smee's batteries may be used to deposit the iron upon copper or brass. The metal in this pure state has a very bright and beautiful silvery appearance. An aqueous solution of cyanide of potassium is a very bad conductor with an iron anode, even if it be maintained hot.

117. *Cobalt Solution.*—To deposit cobalt satisfactorily, dissolve 5 ounces of the red chloride in 1 gallon of distilled water, render the liquid slightly alkaline by cautious additions of aqueous ammonia and stirring, and use a feeble current with a cobalt anode.

118. *Nickel Solutions.*—Since the previous edition of this book was written, the electro-deposition of a thin coating of nickel upon articles of iron, steel, &c., has become an extensive industry. The solution usually employed for nickel-plating is made as follows:—Dissolve from ½ to 1 pound of the *pure* double sulphate of nickel and ammonia in a gallon of distilled water, and filter the liquid. The solution must not be a saturated one. The salt may be obtained of a dealer in electro-plating materials. The liquid must not be in the least degree acid to test paper; and if alkaline, only faintly so;—if acid, add a little aqueous ammonia. Nitric acid or a nitrate must on no account be allowed to get into it. It is used with a large anode of either cast or rolled nickel; anodes of all sizes may be easily purchased ready-made.

Instead of the double sulphate, the double chloride of nickel and ammonium (first suggested and employed by the author of this book *in* the year 1856) has been extensively used in America;—the solution

of it may be prepared as follows:—Dissolve 59 grammes (=about 910 grains) of *pure* nickel in a sufficiency of warm and *colourless* hydrochloric acid. Evaporate the liquid to a small bulk to expel excess of acid; dilute it with about 1 or 1¼ litres (=44 to 55 ounces) of cold distilled water. Add aqueous ammonia to it, with stirring, until it is perfectly neutral or faintly alkaline to neutral tint litmus-paper. Then dissolve 30 grammes (=463 grains) of sal-ammoniac in about 5 litres (=176 ounces or 9 pints) of distilled water, and mix it with the previous solution.

These solutions do not corrode nickel anodes very readily, and are not very good conductors of the current, therefore large anodes are required even when coating small articles. They are liable to become alkaline by continued working, and should be tested occasionally, either with red or neutral tint litmus-paper;—if the paper becomes blue, add (with stirring) a little acid, sulphuric for sulphate baths, hydrochloric for chloride ones. A nickel solution cannot be either too pure or too neutral;—a perfectly neutral and about three-fourths saturated one is the best.

If the liquid is alkaline, the deposited metal is apt to be yellowish and dull in appearance;—too much ammonia also produces a sediment. If it is acid, the deposit remains white and bright, but the coating is apt to be unsound, and in a state of considerable molecular tension. The neutral tint litmus-paper, or the blue and red ones, should be kept in a well-stoppered bottle, and not exposed to fumes. The sulphate or chloride solutions, if properly worked and taken care of, are permanent and will last for years, notwithstanding that a little hydrogen is evolved from the articles during deposition. As these liquids are not good conductors, they do not work freely if they are much below a temperature of 60° Fah. Being also nearly saturated solutions of the salts, they require rather frequent stirring. When plating articles of iron or steel, and especially of zinc, in them, the current should be of greater electro-motive force at the outset for a short time, because those metals are electro-positive to the nickel anodes, and tend to generate an opposing current until they are covered with nickel. A solution of nitrate of nickel is unsuitable for practical deposition of the metal, because the nickel deposited from it is not white.

The vats for containing these nickel solutions may be made of pine-wood, lined with gutta-percha; or lined with lead, and the lead covered with a thin lining of wood pegged together. They should be extra deep on account of liability to disturb, by stirring, the sediment which is apt to accumulate in them. This sediment is caused by the ammonia liberated along with the hydrogen by the action of the current.

The articles to be coated should be absolutely clean, and highly polished, finally, with finely-powdered lime, and the cleaning process

quickly performed. Suitable polishing materials and apparatus are indispensable, because the coated articles also require polishing and the deposited metal is hard and tenacious. The articles must not be touched by the fingers after having been cleaned by the potash, but be handled by means of a wet cloth and the suspending wires, the hands being occasionally dipped in pumice powder.

They are kept in the vat from 5 minutes to 2 or more hours, according to the thickness of the deposit required; for their ordinary coatings they are usually left in until the deposit looks bluish-grey. Thick coatings are apt to scale or peel off, sometimes spontaneously without being touched, in consequence of the molecular strain previously mentioned. A coating of about one-hundredth of a millimetre in thickness can be put on in about 2 hours. By successive operations of polishing and depositing, any desired thickness of coating may be obtained. As the coating is very durable, thick ones are rarely required.

Stout wires of nickel are the best for suspending the anodes, unless the latter project above the liquid. The copper ones by which the articles are suspended must have the nickel which has been deposited upon them frequently removed. To moderate the influence of the current, a thick copper rod (or several of them) is sometimes suspended as a cathode in the vat, and receives some of the deposit;—coatings of nickel, sometimes an inch in thickness, gradually accumulate on these rods.

To remove coatings of nickel from articles of steel or iron which have been defectively plated, the articles are dipped into boiling water and then into a mixture of oil of vitriol 4 litres (=7 pints); nitric acid, 500 grammes (=18 ounces); water, 500 grammes; and saltpetre, 50 grammes. Thin adhesive coatings may be removed from copper by immersion in a mixture of 1 measure of sulphuric acid, 2 of nitric acid, and 4 of water; taking care to first add the sulphuric acid to the water whilst constantly stirring the latter, and then the nitric acid.

As nickel is either corroded or discoloured by wet mustard, infusion of tea, vinegar, solution of table-salt, &c., articles plated with it are not very suitable for cooking utensils, spoons, &c.

119. *Copper Salts.*—The ordinary salts of copper are the protoxide (black oxide of copper), sulphate, chloride, nitrate, acetate, and cyanide. To make the protoxide, heat either the carbonate or nitrate to a moderate red heat, or the sulphate to intense redness. The sulphate may be formed by heating one equivalent (79·5 parts) of copper filings, and at most two equivalents (196 parts) of oil of vitriol, until the residue is quite dry, then dissolving the product in water, filtering, vaporating, and crystallizing the solution; but it is much more con-

venient to purchase it, on account of its low price (4d. to 6d. per pound). The chloride and nitrate may be formed, the first by dissolving copper in aqua regia, or by saturating hydrochloric acid with protoxide of copper, and evaporating and crystallizing the liquids; and the second by dissolving copper in nitric acid, evaporating and crystallizing the solution. Acetate of copper is most conveniently purchased; its commercial name is crystallized verdigris. Cyanide of copper may be made by adding a solution of cyanide of potassium to a solution of sulphate of copper (each liquid being cold) as long as a precipitate can be produced, filtering and washing the precipitate, which is the required compound; it is a fine powder of a pale green colour. In the operation a large quantity of cyanogen gas is evolved, which if freely inhaled is dangerous to the health. In consequence also of this escape of cyanogen the cyanide of copper is not a *proto*-cyanide, but contains two equivalents of cyanogen for every three equivalents of copper; it is freely soluble in a solution of cyanide of potassium; it is also soluble in aqueous ammonia and in a solution of carbonate of ammonia. The proportion of materials we have used in making it has been 65 parts of cyanide of potassium and 125 parts of sulphate of copper. The precipitating solution is invariably greenish-blue, and contains much dissolved copper after all precipitation ceases; but no use has hitherto been made of this remainder.

120. *Copper Solutions.*—Copper may be easily deposited either by simple immersion (wash process), by the single cell, or by the battery process. According to Reinsch, iron may be coated with a durable and polishable layer of copper of any thickness (?) by the simple immersion process thus:—Mix together one measure of hydrochloric acid, three measures of water, and a few drops of a solution of sulphate of copper; clean and immerse the iron; wash it, rub it with the copper solution, and re-immerse it repeatedly, adding a few drops of the copper solution occasionally. In depositing copper by the single cell process, a nearly saturated solution of sulphate of copper answers very well; but for the battery process an excellent solution may be made by dissolving four parts, by weight, of finely divided sulphate of copper (best quality), and one part of sulphuric acid, in about 18 or 20 parts of water, and then filtering it; neither of these solutions, however, is fit to deposit copper upon iron, steel, or zinc; because the electrical relations of these metals in the liquid are unsuitable; these metals decompose the solutions rapidly, and deposit the copper upon themselves by simple immersion. To effect an adhesive deposit of copper upon iron, a liquid composed of cyanide of copper dissolved in a solution of cyanide of potassium may be used. It is formed thus:—Dissolve cyanide of copper to saturation in water containing about two pounds of cyanide of potassium to the

gallon, and then add about one-eighth more of the cyanide of potassium solution to form *free* cyanide; the liquid is then ready, and should be used at a temperature of about 150° Fah.

121. Copper is electro-positive to iron in the following liquids at 60° Fah.:—Powerfully in a solution of hydrosulphuret of ammonia; feebly in a saturated solution of ammonia; in a solution of oxide of copper in liquid ammonia; in aqueous ammonia, or in a saturated solution of ferrocyanide of potassium, each but for a short time—it then becomes negative; in a saturated solution of bichromate of potash; in a strong aqueous solution of sulphide of potassium, it is increasingly positive up to the boiling point of the liquid. This last liquid yielded a similar effect with brass.

122. *Brassing Solutions.*—Much interest and importance was long attached to the discovery of solutions whereby alloys, and especially brass, might be deposited in the reguline state, and various liquids have been used and patented for this purpose. M. de Ruolz, in 1841, deposited brass from the cyanides of zinc and copper, dissolved together in a solution of cyanide of potassium. Copper articles may be superficially brassed by boiling them in a solution of bitartrate of potash with zinc amalgam, or by boiling them in dilute hydrochloric acid with some bitartrate of potash and zinc amalgam.

123. Other early workers in this direction were Russell and Woolrich, whose formula was as follows:—Take 10 pounds of acetate of copper, 1 pound of acetate of zinc, 10 pounds of acetate of potash, and 5 gallons of hot water; dissolve the salts in the water, add as much of a solution of cyanide of potassium as will precipitate the mixture, and re-dissolve the precipitate; in addition add about one-tenth of cyanide of potassium. Use a brass anode, or else two anodes, one of zinc and one of copper, and an electric current.

124. Joseph Steele used the following formula:—Dissolve 2¼ pounds of American potash in 6 gallons of hot water, and filter the solution; also dissolve 2½ ounces of acetate of copper in half a pint of strong liquid ammonia, and add it to the first solution with stirring; also add 4 or 5 ounces of sulphate of zinc, and stir till dissolved; and, finally, add 2 ounces of cyanide of potassium, filter the resulting solution, and use it at 100° Fah., with a brass anode. To obtain a dark coloured brass add more acetate of copper; and to obtain it of a lighter colour, add more sulphate of zinc.

125. Salzede's well-known formula was:—Take 5,000 parts of water, dissolve 12 parts of cyanide of potassium in 120 parts of it, then add 610 parts of sub-carbonate of potash, 48 parts of sulphate of zinc, and 25 parts of chloride of copper to the remainder of the water, and heat the mixture from 144° to 172° Fah.; and when the salts are entirely dissolved, add 305 parts of nitrate of ammonia, allow the

liquid to remain undisturbed for 20 hours, and then add the solution of cyanide of potassium; allow it to remain again till clear, and then draw off the transparent liquid, which is ready for use; work it with a large brass anode and a strong battery. Another liquid which he uses for brassing consists of 5,000 parts of water, 500 parts of subcarbonate of potash, 35 parts of sulphate of zinc, 15 parts of chloride of copper, and 50 parts of cyanide of potassium. For a bronzing solution he uses 25 parts of chloride of tin in place of the sulphate of zinc of the first brassing liquid, and proceeds as with that liquid; for a second bronzing solution he uses 12 parts of chloride of tin in place of the sulphate of zinc of the second brassing liquid, using the solution at 77° to 97° Fah.

126. Brunel, Bisson, and Gaugain's formula consists of 50 parts of carbonate of potash, 2 parts of chloride of copper, 4 parts of sulphate of zinc, and 25 parts of nitrate of ammonia, dissolved together in cold water, which is used with a brass anode and a strong battery.

127. Morris and Johnson's patent, dated December 11, 1852.—According to this patent, dissolve 1 pound of cyanide of potassium, 1 pound of commercial carbonate of ammonia, 2 ounces of cyanide of copper, and 1 ounce of cyanide of zinc, in 1 gallon of water, and use the solution at 150° Fah., with a large anode of brass and a powerful battery. Or a solution may be taken of 1 pound of cyanide of potassium and 1 pound of carbonate of ammonia, dissolved in 1 gallon of water, and saturated with copper and zinc to the requisite degree by means of a strong current, a large brass anode, and small cathode, until the latter receives a good deposit of brass, the solution being at a temperature of 150° Fah. To increase the proportion of copper, either add cyanide of potassium, or raise the temperature of the liquid; and to increase the proportion of zinc, either add carbonate of ammonia or lower the temperature.

128. Of the numerous solutions that have been tried for depositing brass, the one just mentioned is much the best. By it reguline and thick deposits of brass, of uniform colour, and of any desired composition, may be obtained. It is not an expensive liquid; it acts with average strength upon the anode; it holds a sufficient quantity of the alloy in solution; it conducts electricity with moderate facility; and it yields its metal in the reguline state very uniformly; it bears a great variation in the electric power without injury to the character of the deposit, and is, therefore, very easily managed; it does not act perceptibly upon cast iron, wrought iron, steel, or even zinc, so as to injure the adhesion of the deposit; and it is not decomposed by exposure to the atmosphere, to light, or heat, in such a way as to effect its depositing power. Its defects are, that it requires to be worked hot, and with considerable battery power, in order to make

the anode dissolve rapidly, the solution conduct copiously, and to cause a rapid deposit; it also evolves an abundance of gas at the cathode when working, whether the solution is hot or cold, which indicates that part of the battery power is expended in decomposing the water of the liquid, depositing its hydrogen with the metallic alloy, and oxidising the solution. But all the brassing solutions are, in a greater or less degree, imperfect.

Deposition of German Silver.—The same patentees also deposit German silver by the following process:—Dissolve 1 pound of cyanide of potassium and 1 pound of carbonate of ammonia in 1 gallon of water, heat the solution to 150° Fah., immerse a large anode of German silver in the liquid, and a small cathode of any suitable metal, connect the two with a powerful battery, and pass the current of electricity until considerable metal is dissolved and a bright cathode receives a deposit of good colour; the solution is then ready for use.

129. *Mercury Solutions.*—The ordinary compounds of mercury are the bioxide (red precipitate), bisulphide (vermillion), bichloride (corrosive sublimate), nitrate, and bicyanide. The nitrate is formed by dissolving mercury in nitric acid diluted with three times its bulk of water, the mixture being cold, and no more metal added than the acid will dissolve. The solution when diluted with water may be used for depositing by the battery process, a layer of mercury at the bottom of the liquid being used as the anode, and connected with the battery by a platinum wire passing through a tube of glass or gutta-percha. The bicyanide is made by taking 8 parts of Prussian blue and 16 parts of peroxide of mercury, both in the state of fine powder, in 30 parts of water, boiling the mixture for about a quarter of an hour, filtering the liquid, and evaporating and crystallizing the solution; the resulting salt is the bicyanide, and to form it into a liquid fit for depositing, it must be dissolved in a solution of cyanide of potassium; the solution may be used with a mercury anode and battery as already described. It is better to purchase the bicyanide.

130. *Silver Salts.*—The most common salts of silver are the oxide, chloride, nitrate, and cyanide; the oxide, chloride, and cyanide are sold retail at about 7*s.* per ounce, and the nitrate at 5*s.* per ounce. Oxide of silver is prepared by adding a solution of caustic potash to a solution of nitrate of silver, as long as a precipitate can be produced; the brown precipitate, when washed and dried, is oxide of silver. Chloride of silver is made by adding either hydrochloric acid or a solution of common salt to a solution of nitrate of silver, until a precipitate ceases to be formed; the white precipitate of chloride of silver should be washed, dried, and preserved out of the influence of light. Nitrate of silver is easily formed by adding grain silver, in small quantities at a time, to a warm mixture

of 1 measure of distilled water and 4 measures of the strongest nitric acid; if the liquid is too hot, or too much silver is added at a time, the action will be very strong, and loss of materials may be occasioned; in such a case add a small quanity of cold distilled water. When the liquid ceases to dissolve more metal, it should be evaporated and crystallized, or else kept, protected from dust, until required to be used; nearly all the compounds of silver are formed by means of this salt. Acetate of silver is made either by adding a solution of acetate of potash or acetate of soda, to a solution of nitrate of silver, as long as a precipitate occurs, or by digesting the oxide or the carbonate of silver in hot and strong acetic acid; it is freely dissolved by a solution of cyanide of potassium. Cyanide of silver is generally prepared by adding a solution of cyanide of potassium to one of nitrate of silver as long as a precipitate occurs; the white precipitate, which is cyanide of silver, is insoluble in water, and is not preceptibly soluble in commercial hydrocyanic acid; it dissolves very freely in a solution of cyanide of ammonium, potassium, or sodium, and in hyposulphite of soda; it is also said to be soluble in solutions of ammonia, carbonate of ammonia, sal-ammoniac, nitrate of ammonia, and ferrocyanide of potassium.

131. M. Brandeley, a French experimentalist, makes the following remarks upon the preparation of cyanide of silver:—"To obtain a beautiful and easy deposit of silver we choose, among all the salts of silver. the cyanide, as giving the best results; but as the dealers sell this at a high price, both amateurs and manufacturers reject it. Others, for the sake of economy in procuring it, purchase hydrocyanic acid; but this also is of too high a price, and, independently of being obliged to use it immediately, it is both dangerous and difficult to preserve, as the air and light decompose it. If we take commercial hydrocyanic acid which has been prepared fifteen days, and pour it into a solution of nitrate of silver, consisting of 1 part of the nitrate to 6 parts of water, cyanide of silver is formed, but it is more or less yellow, and much ammonia and hydrocyanic gases are evolved. On the other hand, if we make a solution of cyanide of potassium, filter it, and dissolve cyanide of silver in it, immediately the solution, which was clear and colourless, becomes troubled and black, and betrays an odour of ammonia and hydrocyanic acid. This odour will continue as long as the solution exists, and a deposit of carbon will be found in the containing vessel. This sediment arises from the decomposition of one part of the cyanide of potassium, caused by the presence of the cyanide of silver. Having occasion to use considerable quantities of the cyanide of silver, I dissolve pure silver in pure nitric acid, evaporate just to dryness, dissolve the nitrate of silver thus obtained in distilled water, and pass hydrocyanic gas (prussic acid) through it, from a

mixture of pounded ferrocyanide of potassium and sulphuric acid diluted with twice its weight of water, continuing this as long as a precipitate will form. Wash the cyanide of silver, and preserve it below water, away from the light. Thus precipitated, the salt dissolves without residuum or colour, and gives splendid results."

With regard to this process we may remark, that 6 parts of sulphuric acid should be mixed with from 30 to 40 parts of water, and the mixture allowed to cool; then put into a glass vessel (Fig. 35), together with 10 parts of coarsely-powdered ferrocyanide of potassium; and heat applied until gas is evolved from the mixture, and continued as long as gas is evolved, or as long as a precipitate is produced in the silver solution, the gas being passed into the liquid by a suitable tube (see Fig. 35). This process may yield a purer product than when the nitrate solution is precipitated by cyanide of potassium; but it cannot be very economical, because only half of the cyanogen of the ferrocyanide passes over as hydrocyanic acid; the remainder is left behind, and is contained in the yellowish-white residuum in the gas-generating vessel.

Fig. 35.

132. *Silver Solutions.*—Silver has been deposited by the ordinary dipping or wash process, by the single cell, and by the battery process. The following are recipes for solutions taken from various sources, adapted for silvering articles by the simple immersion or wash process, chiefly applicable to small articles, such as pins, buttons, buckles, coffin-nails, hooks and eyes, &c., where only a very thin coating of silver is required. The materials, in the proportions indicated, are used by adding a small quantity of water, sufficient to form the ingredients into a pasty liquid of the consistence of cream, stirring the articles thoroughly about in it, or rubbing them over with it until they have acquired the desired degree of whiteness:—1st. Take equal parts of chloride of silver and bitartrate of potash. 2nd. Take chloride of silver 1 part, alum 2 parts, common salt 8 parts, and tartar 8 parts. 3rd. Take chloride of silver 1 part, prepared chalk 1 part, common

salt 1¼ parts, and pearl-ash 3 parts. 4th. A "novargent" solution for re-silvering old plated goods, consists of 100 parts of hyposulphite of soda, and chloride or any other salt of silver 15 parts. Compounds of this description are also used for silvering clock-faces, thermometer and barometer plates, and many other articles of copper and brass.

133. *Silvering by Immersion.*—Mr. Joseph Steele took out a patent, dated August 9, 1850, for silvering articles by immersing them in a silver solution in contact with a piece of zinc of proper size. The process is as follows:—Dissolve 4 ounces of pure silver in 20 ounces of nitric acid; also dissolve separately 1½ pounds of common salt in 1½ gallons of water; mix the two solutions together, allow the mixture to remain till clear, pour away the clear liquid, and wash the precipitate, which is chloride of silver; next fuse together 24 ounces of ferrocyanide of potassium and 12 ounces of carbonate of potash, and when the mass is cold, add it, together with the chloride of silver, to 1½ gallons of water; boil the mixture, and filter it; it is then ready for use.

134. *Silvering Solution for Battery Process.*—Many solutions have been proposed and tried for depositing silver by the battery process, but none have stood the test of time and experience like the one composed of double cyanide of silver and potassium dissolved in water, and a little *free* cyanide of potassium added. It may be made of various strengths, from ½ an ounce of silver to the gallon of water, to 2, 4, 6, or more ounces; and from an ounce of cyanide of potassium to several pounds per gallon, and still be effective in working. The formula of M. de Ruolz is as follows:—Dissolve 1 part of cyanide of silver and 10 parts of cyanide of potassium in 100 parts of water, and dilute the resulting liquid with water to the required strength.

135. *Silver Plating Solution.*—The following is the most practical method of making a large quantity of the ordinary cyanide of silver-plating liquid:—Take 4 parts of grain silver, add it, in small portions at a time, to a warm mixture of about 5 parts by weight of strong commercial nitric acid (the acid varies a little in strength), and 1 part of water, contained either in a glass or stoneware vessel. Gas will be evolved from the surfaces of the pieces of silver, and brown fumes of nitrous acid will arise from the mixture, which should be conveyed out of the apartment by means of the chimney. The action should be maintained moderate and uniform, and if it should become too strong, a little cold water should be added, and the mixture kept cooler; when the whole of the metal is dissolved, apply a greater heat, and evaporate the solution to a small bulk, which will drive off any excess of acid that may be present; the resulting salt, nitrate of silver, may then be dissolved in a large quantity of water, in the proportion of ½ gallon (more or less) to each ounce of silver used; at

the same time a solution should be made of from 3 to 3¼ parts (according to its quality) of cyanide of potassium in 30 or 40 parts of water, which is to be added gradually, with stirring, to the one of nitrate of silver as long as it produces a precipitate; if too much be added, it will cause some of the precipitate to re-dissolve and be wasted; it will also make the liquid appear clear where it passes; in such a case the liquid should be stirred, then allowed to settle clear, and a small quantity of nitrate of silver dissolved in *distilled* water should be added as long as it produces a white cloud. By conducting the operation in a glass vessel, adding the liquid towards the latter period in small quantities at a time, and at intervals of a few minutes each, with gentle stirring immediately upon each addition, carefully observing when it ceases to produce a precipitate, the point of neutralization may be very accurately determined. The liquid must now be allowed to remain undisturbed until quite clear, the clear portion poured steadily away from the precipitate of cyanide of silver, and the precipitate washed five or six times in a large quantity of water, by simply adding the water briskly to it, allowing it to settle, and then pouring away the clear portion. Next dissolve from 3 to 3¾ parts (according to its quality) of cyanide of potassium in 20 parts of water, adding it in portions at a time to the wet cyanide of silver, with free stirring, until the whole is dissolved, then add about 3 parts more of cyanide of potassium to form *free* cyanide, and sufficient water to reduce the whole to the proportion of about 1 ounce of silver to the gallon; finally, when all the free cyanide is dissolved, filter the solution through a piece of unglazed calico. Distilled water is used in all cases. The wash-water should be tested for silver by a little hydrochloric acid, before throwing it away.

136. *Another Solution.*—The cyanide of silver-plating solution may be made by other modifications of the chemical method than the one described. For instance, some depositors make the solution by adding oxide, carbonate, or even chloride of silver to a solution of cyanide of potassium, as long as it will dissolve, and then adding an amount of free cyanide; by this process the operator is enabled to use caustic potash, carbonate of potash, hydrochloric acid, or common salt, instead of cyanide of potassium, for precipitating the nitrate of silver; nevertheless it still requires two equivalents of cyanide of potassium to be used as before, viz., one to convert the salt of silver into cyanide, and the other to dissolve the cyanide of silver formed, because in all such cases, according to the researches of Messrs. Glassford and Napier ("Philosophical Magazine," 1844), when any salt of silver is added to a solution of cyanide of potassium, it is first converted into cyanide of silver at the expense of one portion of the cyanide of potassium; it then combines with the remaining cyanide to form double cyanide of

silver and potassium, which dissolves in the water; therefore, by this modification of the chemical method, no cyanide of potassium is saved, and the carbonate of potash, hydrochloric acid, &c., are wasted. This modification has a still greater disadvantage; it introduces substances into the depositing liquid which are injurious. We have before said (§ 90) that a good depositing solution should dissolve the anode freely, hold abundance of metal in solution, and not act chemically upon base metals, because it is such metals we generally wish to coat; now, if we add carbonate of silver, it converts it into carbonate of potash; if instead of cyanide of silver we add oxide of silver to the cyanide of potassium liquid, it converts part of the cyanide into caustic potash; and if chloride of silver, it converts it into chloride of potassium; and each of these substances, especially the last, diminishes the action of the liquid upon the dissolving plate, decreases its solvent power for cyanide of silver, makes its particles less mobile, and causes it to act in some degree upon base metals, and thus endangers the adhesion of the deposits upon them. Some electro-platers think the presence of these salts not injurious, but most consider them detrimental.

137. *Solution by Battery Process.*—The same silver solution may be formed by the battery process (§ 89) as well as by the chemical method, and this process has its own advantages and disadvantages; it is very convenient in making a small quantity of liquid, because it enables the operator to make it quickly, to avoid the trouble of making the nitrate solution, of precipitation, of washing, and of the attendant risk of loss of materials; but it has the disadvantage of converting a large proportion of the cyanide of potassium into caustic potash, by taking its cyanogen to form cyanide of silver, and setting the potassium free, which immediately combines with the oxygen of the water, forming caustic potash, which dissolves in the liquid; whilst the hydrogen of the water is evolved at the cathode, and the dissolved potash gradually becomes converted into carbonate of potash by absorption of carbonic acid from the atmosphere. Neither caustic potash nor carbonate of potash are so injurious in the liquid as chloride of potassium; still they diminish the action of the liquid upon the dissolving plate, render it a worse conductor, reduce its solvent power for cyanide of silver, and make its particles less mobile.

138. *Solid Deposition of Silver.*—Mr. Alexander Parkes took out a patent, March 29, 1841, for improvements in the solid deposition of silver. He converts an ounce of silver into oxide of silver, by first dissolving it in nitric acid, and then precipitating it by caustic potash; he then dissolves the oxide together with 16 ounces of cyanide of potassium in 2 gallons of water, and uses the resulting liquid for depositing solid articles in silver.

139. Mr. Edmund Tuck not very long after introduced some "im-

provements in deposting silver upon German silver." For plating the commoner qualities of this alloy he uses a solution composed of sulphate of silver dissolved in a solution of carbonate of ammonia, and for the best quality he uses cyanide of silver dissolved in a solution of carbonate of ammonia. The solutions are formed by dissolving 70 parts of carbonate of ammonia in distilled water, then adding 156 parts of sulphate of silver, or 134 parts of cyanide of silver, and boiling the liquid until the salt is dissolved; for coating common German silver he adds half an ounce of sulphate of silver to 107 grains of bicarbonate of ammonia.

140. For depositing purposes, a solution composed of water 20 parts, cyanide of potassium 4 parts, and acetate of silver 1 part, conducts very freely, and yields a fine white deposit of silver. A solution composed of water 25 parts, prussic acid 65 parts, "black" cyanide of potassium 12 parts, and cyanide of silver 10 parts, is also a very good one.

141. Many electro-platers use a cyanide solution containing about half an ounce of silver to the gallon, and add a very large proportion of free cyanide to make it conduct freely; such a solution has the advantage of being comparatively inexpensive in its first formation, quick in working, and yields metal of an average character; but it is rather difficult to manage in hot weather, and dissolves the anode very rapidly, on account of the large proportion of free cyanide. In practice, the amount of silver to the gallon varies from half an ounce to about 4 ounces, but ordinary solutions contain about 1 or 2 ounces to the gallon; the amount of *free* cyanide of potassium also varies from about half the weight of the silver dissolved in the liquid to five or ten times this quantity. A very good proportion is about three-fourths of the weight of the dissolved silver, but there is no rule generally recognised in the trade upon this point; some manufacturers use a very large and others a very small proportion.

142. A good plating liquid should contain one equivalent (65 parts) of pure cyanide of potassium, and one equivalent (134 parts) of cyanide of silver, besides *free* cyanide, and sufficient water to form a thin liquid. It is necessary to have *free* cyanide, because in working the solutions insoluble cyanide of silver is formed and requires *free* cyanide of potassium to combine with it and form the soluble double cyanide; at the same time cyanide of potassium is set free at the cathode or receiving surface by the deposition of the silver, and as it requires some time for this substance to mix with the liquid and reach the dissolving plate, *free* cyanide must be provided. The necessity for having sufficient water to form a *thin* liquid arises from the double cyanide formed at the dissolving plate being specifically heavier than the liquid, having a tendency to sink to the bottom, whilst

the cyanide of potassium set free at the surface of the articles, being specifically lighter, tends to rise to the surface; at the same time each of them mixes more or less with the surrounding liquid by capillary attraction or adhesion, and the more dilute the liquid is the more mobile are its particles, and the more rapidly does this mixture take place. This explains why strong silver solutions require more frequent stirring than weak ones to keep them uniform. In some manufactories, where they have steam-power at command, the articles are kept in constant motion by machinery swinging them gently to and fro; but in ordinary electro-plating establishments the silver solutions are only stirred every evening.

143. If a solution contains but little water and a large supply of free cyanide, and from any cause the electric current becomes suddenly weak towards the evening, the silver deposited upon the articles will be re-dissolved, in consequence of the liquid about the dissolving sheets having by the day's work become saturated with silver, and that about the articles become full of free cyanide; the two electrodes (*i.e.*, the dissolving plates and the articles) form a kind of voltaic battery (one metal in two liquids), which develops a current of electricity in an opposite direction to the original one, and thus re-dissolves the deposited silver.

144. *Bright Silver Solution.*—Much practical interest was for a long time attached to the anticipated discovery of a solution by which silver might be deposited in a *bright* condition, and the labour of burnishing be thereby avoided or lessened; and this discovery was at last effected as follows:—Mr. Alexr. Parkes, at the electro-plate works of Messrs. Elkington and Mason, Birmingham, was engaged in some experiments with moulds containing bisulphide of carbon; whilst these moulds were being coated with silver in the depositing vats, the depositor observed some peculiar appearances upon the various articles receiving a deposit in the vat, some having bright patches upon them like burnished metal. From the known presence of bisulphide of carbon, experiments were made of adding that substance to a quantity of silvering liquid, which ultimately resulted in success, and a patent was taken out for this process by Messrs. Lyons and Millward, in which they give the following instructions for forming a "bright solution":—"Add to the usual solution of silver in cyanide of potassium, bisulphide of carbon, terchloride or other chloride of carbon, sesquichloride of sulphur, or hyposulphite of either potash or soda. The bisulphide of carbon may be used alone or dissolved in sulphuric ether; or it may be used in conjunction with any of the other substances mentioned above, but the patentees prefer using it as follows:—6 ounces of bisulphide of carbon are put into a stoppered bottle, and 1 gallon of the usual plating liquid added to it;

the mixture is then shaken and set aside for 24 hours; 2 ounces of the resulting solution are then added to every 20 gallons of the ordinary plating solution in the vat, and the whole stirred together; this proportion must be added every day, on account of the loss by evaporation, but when the mixture has been made several days, less than this proportion may be used at a time; when hydrocarbons are used instead of the bisulphide, a much larger quantity must be added. This proportion gives a bright deposit, but by adding a larger proportion a dead surface may be obtained, very different to the ordinary dead surface." This substance is generally employed throughout the trade, the patent having expired. Other compounds are also used, but to a very limited extent: among these are sulphur and collodion. A solution of iodine and gutta-percha in chloroform is said to be more permanent in its effect than the bisulphide of carbon. The liquid is generally added to the vat in the evening after the work has been taken out. A method of bright *gilding* has also been brought into use in the trade.

145. *Method of Making Cyanide of Potassium.*—As nearly all the solutions which are used for electro-silvering and gilding contain cyanide of potassium, and as this substance is used extensively in electro-deposition generally, it will be necessary for the practical depositor to understand how it is made, and to possess information respecting its impurities, and the method of testing its quality. It is nearly always made by the following process:—Take ferrocyanide of potassium (yellow prussiate of potash), pound it fine, and gently heat it in an iron pan, with constant stirring until quite dry; treat a quantity of the best quality of carbonate of potash in a similar manner. When they are perfectly dry, add about 3 parts of the carbonate to 8 parts of the ferrocyanide, and thoroughly mix them; heat the mixture rapidly in an iron ladle or crucible, until it melts into a clear liquid, when gas will be evolved from its surface. It should be maintained at a moderate or dull red heat about 15 or 20 minutes, or until the end of a cold iron rod dipped into it shows a white sample. The fusion should not be continued until the evolution of gas ceases, or the product will be of a grey colour. It should be kept covered as much as possible. By allowing it to stand undisturbed for a few minutes at the latter part of the operation, and occasionally tapping the sides of the ladle or crucible, the iron of the ferrocyanide will settle at the bottom as a fine black powder; the colourless cyanide of potassium may then be poured off into a cold iron pan, or upon a thick and cold iron plate; it should be broken up whilst still warm, and preserved in a well-stopped jar.

The black sediment, which contains much cyanide of potassium, should be scraped out of the vessel while still hot, and preserved, as

water will at any time dissolve the cyanide. If the process has been well conducted, the product will be of a clear white colour, or at most but very slightly grey. A larger proportion of cyanide of potassium is obtained by this process than when ferrocyanide alone is employed, because in the former case one-third of the cyanogen (that which was combined with the iron) combines with the potassium of the carbonate of potash, whilst in the latter case it is lost; the cyanide produced by the fusion of the ferrocyanide of potassium alone is of a greyish-black colour, and is termed "black cyanide."

146. *Cyanide of Potassium.*—Commercial cyanide of potassium varies very much in price; the best quality of white cyanide is sold retail from 2*s.* 6*d.* to 4*s.* 6*d.* per pound in England; in the United States of America it varies from 2*s.* 3*d.* to 2*s.* 6*d.* per pound, according to quality; and black cyanide may be obtained retail at 3*s.* 10*d.* per pound. By dissolving several specimens of commercial black cyanide in water, and filtering the solution, we found the proportion of black impurity in them varied from one-fourth to one-sixth of their weight; and by experiments with the commercial white cyanide we found that 1 part (200 grains) of it dissolved in about 1¼ parts (230 grains) of distilled water at 60° Fah., and that it dissolved more freely in water containing hydrocyanic acid.

147. *Impurities in Cyanide of Potassium.*—According to the researches of Messrs. Glassford and Napier ("Philosophical Magazine," 1844), commercial white cyanide generally contains about 35 per cent. of impurities, and as often as much as 50 per cent., in the form of carbonate and sulphate of potash, chloride of potassium, cyanate of potash, ferrocyanide of potassium, and silica; and if the mixture of salts from which it is made is not dry, ammoniacal compounds are also formed. The sulphate of potash and chloride of potassium occur in the commercial carbonate of potash; the silica is present when we operate with an earthen crucible; and even when the process is well conducted and pure materials used, the product contains 20 per cent. of cyanate of potash, produced partly by the contact of the air with the melted mixture.

148. *Testing Cyanide of Potassium.*—According to the same experimentalists, the quantity of pure cyanide in any given sample of cyanide of potassium may be correctly ascertained thus:—Make two solutions, one of the given cyanide and one of nitrate of silver, each containing known weights of the salts, say 1 ounce of the cyanide dissolved in 6 ounces of distilled water in a graduated glass vessel, and 175 grains of the crystallized nitrate dissolved in about 2 or 3 ounces of distilled water; add the cyanide solution carefully and slowly to the nitrate of silver liquid, until the precipitate first formed is all re-dissolved. The quantity of the cyanide solution required to effect this (with the above

quantity of nitrate of silver) will have contained 130 grains of pure cyanide, and from the quantity used we may easily calculate the amount of pure cyanide in the whole ounce. It is said, that "when nitrate of silver is added to a solution of cyanide of potassium, so long as the precipitate formed is all re-dissolved, we obtain the *whole* of the cyanide of potassium in combination with the silver; none of the other salts in solution take any part in the action, even though they be present in a large proportion. This enables us to test the exact quantity of cyanide of potassium in any sample."

149. *Chemical Characters of Cyanide of Silver.*—In the presence of cyanide of potassium, so we are informed by Messrs. Glassford and Napier, cyanogen has a greater affinity for silver than anything else has, decomposing every salt of silver except the sulphide, and forming cyanide of silver. In dissolving the oxide, carbonate, chloride, or ferrocyanide of silver, in a solution of cyanide of potassium, they are all decomposed, and cyanide of silver always formed. Cyanide of silver should be dried below 260° Fah.; hydrochloric acid decomposes it with evolution of hydrocyanic acid gas; cold nitric acid has no action upon it; a boiling mixture of sulphuric acid and water decomposes it, with escape of hydrocyanic acid gas, and formation of sulphate of silver; it is soluble in the alkaline chlorides, but its best solvent is an aqueous solution of cyanide of potassium, of which it requires 1 equivalent (65 parts) to dissolve one equivalent (134 parts). The resulting solution, when evaporated, yields crystals of double cyanide of silver and potassium, which are soluble in 8 parts of cold or in 1 part of boiling water. The solution of this double salt, which is nearly the same as the ordinary plating solution, may be boiled for any length of time without being decomposed, and it is very little affected by light; it is decomposed by nearly all acids—they precipitate the silver as cyanide of silver; the hydro-acids—hydrochloric acid, for example—decompose the cyanide of silver also; sulphuretted hydrogen precipitates the silver as sulphide of silver.

150. **Gold Solutions.**—Various salts of gold have been used for electro-deposition, among which are the hyposulphite, sulphite, iodide, bromide, terchloride, cyanide, and sulphocyanide. Finely-divided gold, which is sometimes used for dissolving, may be obtained by adding a solution of protosulphate of iron to a solution of terchloride of gold, as long as a greenish-brown precipitate occurs; this is gold in a state of very minute division. Oxide of gold is obtained by adding to a solution of terchloride of gold a cold solution of caustic potash, until it ceases to produce a precipitate; or by digesting terchloride of gold with magnesia; washing the latter precipitate, first with dilute nitric acid and then with water only. Iodide of gold is formed, either by digesting oxide of gold in hydriodic acid, or by adding a solution of

iodide of potassium to a solution of terchloride of gold as long as a precipitate is produced, washing the precipitate with water; it is of a yellow colour, insoluble in cold water, but freely soluble in a solution of iodide of potassium. Bromide of gold may be formed either by digesting finely-divided gold, or oxide of gold, in liquid bromine contained in a stoppered bottle. It is a salt of a rich red colour, and is soluble in water. It is difficult to make pure oxide of gold.

151. *Chloride of Gold.*—Terchloride of gold, commonly known as chloride of gold, is the most useful salt of the metal, and its preparation requires separate explanation. It is formed as follows:—Take a mixture of either two or three measures of hydrochloric acid, and one measure of nitric acid; warm the mixture, and add pure grain gold to it as long as it will dissolve; it evolves gas whilst dissolving. When it is all dissolved, slowly evaporate the liquid until it crystallizes to a dark ruby red mass, or it may be of a yellow colour, according to the proportions of the ingredients. This is terchloride of gold, and contains one equivalent (196 parts) of gold, and three equivalents (106·5 parts) of chlorine; if it is too much evaporated, chlorine gas will be evolved, gold will be set free and be mixed with the salt, and will precipitate on dissolving the salt in water. To produce the *yellow* chloride, mix together, in a glass or stoneware vessel, 1 part by weight of nitric acid, 3 parts of hydrochloric acid, 1 part of fine gold, and 1 part of water; cover the vessel with a glass dish, make the liquid quite hot, and maintain the heat until the red vapours cease; if some of the gold remain undissolved, add more of the liquid mixture, and treat as before; when the vapours cease, remove the glass cover, and replace it by folds of blotting paper, and evaporate until it crystallizes on *cooling* into yellow chloride of gold. The red chloride is formed in the same manner, except that the liquid mixture should be composed of 1 part of nitric, and 2 parts of hydrochloric acid, more being added than is necessary to dissolve all the gold. One ounce of gold will dissolve in about 4 ounces of the mixture, and when crystallized into the red mass, will weigh about 1 ounce and 165 grains.

152. *Cyanide of Gold.*—"Cyanide of gold is formed by cautiously adding a solution of cyanide of potassium in 6 parts of water, to a normal solution (*i.e.*, not containing any *free* acids) of terchloride of gold, consisting of 1 part of the chloride and 5 parts of water, until a copious yellow precipitate settles down; if more cyanide of potassium is added, the precipitate becomes dirty yellow, and is more quickly deposited; a still larger quantity renders it orange yellow. It is a crystalline powder, permanent in the air. By ignition it is resolved into gold and cyanogen gas; it is not decomposed by sulphuric, hydrochloric, or nitric acid, nor by aqua regia, unless freshly precipitated, and then only slowly. It is not decomposed by sul-

phuretted hydrogen; hydrosulphide of ammonium dissolves it slowly but completely, forming a colourless solution, from which, by the addition of acids, sulphide of gold is precipitated. It dissolves in aqueous solutions of ammonia, hyposulphite of soda, or alkaline cyanides; but not in water, alcohol, or ether."

153. "Gold precipitated from a solution of chloride of gold by protosulphate of iron, dissolves in a boiling solution of cyanide of potassium; a hot solution of cyanide of potassium will also dissolve ordinary metallic gold if air be present. Both oxide of gold and aurate of ammonia dissolve completely in a solution of cyanide of potassium, and form double cyanide of gold and potassium. Cyanide of gold requires 23 parts of cyanide of potassium dissolved in water to dissolve it. For every 1 part of gold to be dissolved by the battery process, 6 parts of cyanide of potassium dissolved in from two to four times their quantity of water, at 100° Fah., are required, two electrodes of gold being connected with a suitable battery, and immersed in it until the required quantity of gold is dissolved."—"The crystallized cyanide of gold and potassium dissolves in 7 parts of cold, and in half a part of hot water (*Himly*); in 4 parts of cold and in 0·8 parts of hot water (*Glassford and Napier*). It dissolves very sparingly in alcohol. Its aqueous solution gilds copper and silver by simple immersion, especially if hot, and the copper and silver dissolve in it."

154. *Gilding by Immersion.*—The following solutions have been used for gilding by the simple immersion, or "water-gilding" process:—1st. Dissolve 5 troy ounces of grain gold in 52 avoirdupoise ounces of hot aqua regia until vapours cease to be evolved. Decant the clear liquid when cool, dilute it with 4 gallons of distilled water, add 20 pounds of purified bicarbonate of potash, and boil it for two hours. The articles to be gilt are immersed in the liquid from a few seconds to one minute, according to the kind of metal immersed, and the temperature and newness of the liquid; warmth assisting the action, and a new liquid acting more quickly than an old one. 2nd. For gilding silver articles, dissolve equal parts of bichloride of mercury (corrosive sublimate) and sal-ammoniac in nitric acid; add pure gold to it, and evaporate the liquid by heat to half its volume. Apply the liquid whilst hot to the surface of the article.

155. Joseph Steele's patent, dated August 9, 1855.—Dissolve an ounce of gold in a mixture of 4 ounces of hydrochloric acid and 8 ounces of nitric acid, and evaporate the solution to dryness. Fuse together 24 ounces of ferrocyanide of potassium and 12 ounces of carbonate of potash; when it is nearly cold, dissolve it in 2 or 3 gallons of pure boiling water, cool and filter the solution, then add the chloride of gold, and boil it for a quarter of an hour. The articles to be coated are connected with a piece of zinc of suitable

size, and immersed in the liquid, the latter being at a temperature of 80° or 85° Fah.

156. *Gold Solutions for the Battery.*—For the battery process there are many gold solutions, though but few good ones:—1st. The hyposulphite of gold and soda, which is formed by dissolving chloride of gold in a solution of hyposulphite of soda; it is not considered a good liquid for practical purposes. 2nd. The sulphite of gold and potash, formerly used by Mr. Woolrich, was made by adding sulphite of potash to water, saturating five-sixths of the resulting liquid with oxide of gold, and then adding the other portion of solution to form *free* sulphite. 3rd. The terchloride of gold dissolved in water; it is a very inferior liquid for practical purposes, because all the common metals decompose it. 4th. The bromide of gold proposed by Mr. Spencer; his solution was made as follows:—"Make a mixture of equal parts of bromine and alcohol, and of this mixture take 1 part, of acetic acid 1 part, and 4 parts of water containing a few drops of sulphuric acid." The resulting liquid is then nearly saturated with gold by suspending it in 2 electrodes of gold, and connecting them a sufficient time with a suitable battery; when nearly saturated, add to the solution three times its volume of water containing a few drops of sulphuric acid.

157. *Electro-Gilding Liquid.*—The best liquid that has as yet been tried for practical electro-gilding is the double cyanide of gold and potassium dissolved in water. It was invented by Mr. Wright, and first patented by Elkington; it may be formed either by dissolving any salt of gold in a solution of cyanide of potassium; or by the battery process, by suspending two electrodes of gold in a solution of cyanide of potassium, and passing a current from a small battery until the cathode receives a proper deposit, the liquid being at about 100° or 150° Fah.

158. *Cyanide of Gold Solution by Chemical Process.*—The cyanide of gold and potassium solution is occasionally made by the chemical plan, as follows:—Form some terchloride of gold (§ 151), and dissolve it in water; then either add a cold solution of caustic potash as long as a precipitate is produced, filtering and washing the precipitate with distilled water; or digest the diluted chloride solution with magnesia; filter, and wash the precipitate with dilute nitric acid and then with distilled water; or add to the chloride liquid a solution of carbonate of ammonia, until a precipitate ceases to be formed; filter, and wash the precipitate with water. The precipitates produced by potash or by magnesia consist of oxide of gold; whilst those produced by ammonia, or its carbonate, are aurate of ammonia (fulminate of gold), *a very explosive compound.* The precipitate, after being well washed by the successive additions of clean water, should be added, whilst still

wet, to a solution of cyanide of potassium, containing the proportion of 1 pound of cyanide to 1 gallon of water, and then about one-fifth more of the same solution should be added to form *free* cyanide. A very good proportion of the ingredients is, 1 ounce of gold, 1 pound of cyanide of potassium, and 1 gallon of water. The wash-waters should not be thrown away without first being tested for gold, by immersing a piece of bright zinc in them, and observing if it receives a metallic film; if it does, a solution of protosulphate of iron should be added as long as a precipitate of a greenish-brown powder, which is metallic gold, is produced. If this fails to precipitate the whole of the gold, a sheet of bright zinc should be immersed in the liquid, taken out occasionally, and the deposit of gold brushed off by a hard brush in water containing a little sulphuric acid. The greater the quantity of *free* acid contained in the original chloride solution, and the larger the excess of potash, ammonia, or carbonate of ammonia added, the greater is the amount of gold dissolved in the wash-waters. If, when we dissolve the terchloride of gold in water, a yellow powder remains undissolved at the bottom of the vessel, it indicates that there is no free acid in the salt, and may be re-dissolved by the addition of a small quantity of the mixture of nitric and hydrochloric acids with application of heat.

159. *Solution by Battery Process.*—A good solution is best made by the battery process, thus:—Dissolve some cyanide of potassium in hot distilled water, in the proportion of from 1 to 2 pounds to the gallon; nearly fill a small porous cell with the liquid, and immerse it nearly to its edge in the solution; place a large gold anode in the outer liquid and a small platinum cathode in the liquid of the porous cell, and connect them with about 3 pairs of Smee's batteries—the gold anode with the platinized silver by 1 wire, and the platinum cathode with the zinc by another, allowing the current to pass, until, by transferring the cathode for a short time to the outer liquid, it receives a good deposit of gold, the solution being maintained at a temperature of about 150° Fah.; the liquid of the porous cell should then be transferred to the outer solution and the process stopped. The amount of gold dissolved is not of material consequence provided the deposit is good, as a solution may contain from half an ounce to 4 ounces to the gallon and be a good depositing liquid.

160. *Gilding Solution of M. Ruolz.*—"Dissolve 10 parts of cyanide of potassium in 100 parts of distilled water; filter it, and add 1 part of cyanide gold, prepared with care, well washed, and dried out of the influence of light; keep the mixture in a closed glass vessel, at the temperature of 60° to 70° Fah. for two or three days, out of the presence of light, with frequent stirring."

161. *M. Becquerel's Gilding Liquid.*—"Dissolve 1 part of terchloride

of gold and 10 parts of ferrocyanide of potassium in 100 parts of water; filter the liquid, to remove the separated cyanide of iron; add 100 parts of a saturated solution of ferrocyanide of potassium, and dilute the mixture with once or twice its volume of water. In general the tone of the gilding varies according as the solution is more or less dilute; the colour is most beautiful when the liquid is most dilute, and most free from iron. To make the surface appear bright it is sufficient to wash the article in water acidulated with sulphuric acid, rubbing it gently with a piece of linen cloth."

162. *Gilding Liquids of M. Fizeau.*—"1st. Dissolve 1 part of dry chloride of gold in 160 parts of distilled water; then add, little by little, a solution of carbonate of potash in distilled water until the liquid begins to become cloudy; we may use this liquid immediately. And, 2nd, used by M. Lerebour:—Dissolve 1 gramme of chloride of gold and 4 grammes of hyposulphite of soda in 1 litre of distilled water."

163. *M. Levol's Solution for Gilding Silver.*—"Dissolve neutral chloride of gold in water, then add a solution of sulphocyanide of potassium, until the precipitate first formed is re-dissolved. The liquid will retain a slightly acid reaction; if it has lost it, it must be renewed by adding a few drops of hydrochloric acid."

164. *By M. De Briant.*—"Dissolve 34 grammes of gold in aqua regia, and evaporate the solution until it becomes neutral chloride of gold; then dissolve the chloride in 4 kilogrammes of warm water, and add to it 200 grammes of commercial magnesia, carefully sifted. The gold is precipitated in union with the magnesia; filter and wash with pure water; digest the precipitate in 40 parts of water mixed with 3 parts of nitric acid to remove the magnesia; then wash the oxide of gold remaining with water, until the wash-water exhibits no acid reaction. Next dissolve 400 grammes of ferrocyanide of potassium, and 100 grammes of caustic potash in 4 litres of water, add the oxide of gold, and boil the solution about 20 minutes. When the gold is dissolved there remains a small amount of iron precipitated, which may be removed by filtration, and the liquid, of a fine gold-yellow colour, is ready for use. It may be used either hot or cold."

165. *Formulas of M. J. L.*—"1st. Take 31 grammes and 25 centigrammes of oxide of gold, 5 hectogrammes of cyanide of potassium, and 4 litres of water, and boil them together half-an-hour. The resulting solution must be worked hot, and may be used to gild copper, brass, and silver. 2nd. Dissolve 10 parts of ferrocyanide of potassium and 1 part of dry terchloride of gold in 100 parts of water, oxide of iron will be precipitated. Boil the solution 2 or 3 hours, in a porcelain or glass vessel, until a precipitate collects at the bottom and the supernatant liquid is transparent and of a canary-yellow colour; filter

the solution, and dilute it with 3 times its volume of water."—One hectogramme equals $3\frac{1}{2}$ ounces. A litre equals $1\frac{3}{4}$ pints.

166. A process or branch of trade termed "solid depositing" has gradually extended itself. It consists in making solid articles of gold and silver, by electro-deposition, upon gutta-percha or other moulds—such, for instance, as watch and clock faces, ornamental snuff boxes, and other articles elaborately chased or engraved, or which have very complex or undercut ornaments upon them; the expense of multiplying these by the electro-process being less than by the ordinary means. Mr. Alexander Parkes, early in the history of deposition, patented a solution for depositing solid articles in gold; it is formed thus:—Dissolve 1 ounce of pure gold in aqua regia, and evaporate the solution to dryness; then add 2 gallons of water and 16 ounces of cyanide of potassium, and work the resulting liquid at a temperature of about 120° or 130° Fah.

167. *Salts of Platinum.*—The only common salt of platinum is the bichloride; it is formed by adding pieces of platinum-foil to hot aqua regia as long as gas is evolved from them; the solution, which is then of a deep red colour, should be evaporated nearly to dryness and left to cool.

168. *Platinum Solutions.*—For platinizing silver by simple immersion process, we may use a solution consisting of bichloride of platinum, dissolved in water containing one-fourth its volume of nitric acid, or we may use simply a very hot aqueous solution of the bichloride alone. Nearly all metals decompose the bichloride solution, and become coated with platinum in it by simple immersion. For the battery process we may use solutions of the iodide, bromide or bichloride, or of the double chloride of platinum and sodium. The solution of the double chloride of platinum and sodium is made by dissolving 1 equivalent (268· parts) of bichloride of platinum and 1 equivalent (58·5 parts) of common salt, in water; it requires a small anode of platinum and a very weak battery to obtain a reguline deposit. A solution for depositing reguline platinum may also be made by dissolving bichloride of platinum and common salt in a solution of caustic potash.

169. *Palladium Solutions.*—A solution of double cyanide of palladium and potassium may be used for depositing palladium. It may be made by chemical means, by dissolving palladium in nitric acid, precipitating the liquid by a solution of cyanide of potassium, washing the precipitate, and dissolving it in a solution of cyanide of potassium to saturation, and then adding a little free cyanide; or it may be easily made by the battery process, by passing a current through a large palladium anode in a solution of cyanide of potassium, until a clean *smooth cathode* receives a good deposit. This is an excellent solution

for depositing coherent metal; it acts upon the anode with uncommon energy, conducts freely, and deposits plenty of reguline metal of easy management; a thin deposit of palladium obtained in this solution has been used for fixing Daguerreotype pictures, instead of gold, and is said to give them a finer tone.

170. *Selected Practical Liquids.*—Having enumerated all the solutions which have been used for depositing different metals, and described the modes of forming them, we now offer a selection of those which are in most general use in the trade:—

1st. For depositing zinc, which is not very often attempted, the sulphate solution (§ 105) may be used.

2nd. For depositing copper, by the battery process, upon all ordinary metals except zinc, tin, lead, iron, and steel, and upon gutta-percha, wax, and elastic moulds, after having been made conductible, the sulphate solution (§ 120) is in general use; but for surfaces of tin, lead, iron, or steel, the solution of cyanide of copper and cyanide of potassium (§ 120) is employed.

3rd. For the deposition of brass upon all ordinary metals, the patented solution of Messrs. Morris and Johnson (§ 127) is very successfully used; the solutions of Brunel (§ 126) and Salzede (§ 125) are also in practical use; and, in the United States of America, a solution very similar to that of Messrs. Morris and Co. is employed.

4th. For depositing silver upon all common metals, the solution of double cyanide of silver and potassium (§ 135) is almost universally used; the only exception is where the double sulphite of silver and potash is used, but only to a small extent, the dynamo-electric machine being generally employed with it.

5th. For gilding all ordinary metals, the only liquid extensively employed is the cyanide of gold and potassium (§ 157 and § 158), the exceptions being a few minor modifications of it in private use.

6th. For platinizing, the only liquid of practical value is the bichloride (§ 167.)

7th. For *solid* deposition of silver and gold, the patented solutions of Mr. Alexander Parkes (§ 138 and § 166) may be employed.

171. **Cleaning Metals for Receiving a Deposit.**—The electro-depositor having acquired a general knowledge of depositing liquids, as well as of the requisite manipulation, and having made the several solutions necessary for his ordinary use, will require to prepare his articles for receiving a deposit. All metallic articles must be perfectly cleaned and otherwise prepared before they are fit to receive a coating; this preparation differs, of course, according to the nature of the article, whether the coating is required to adhere firmly to the surface, or is merely used as a matrix, from which the deposited metal is to be removed.

172. *Cast Iron and Zinc.*—Articles formed of zinc, wrought iron, cast iron, or steel, are first immersed a few minutes in a boiling solution of caustic potash to remove any grease, tar, or oily substance which may be upon them; they are then washed in water, and those of wrought or cast iron are immersed in "pickling liquid" (§ 82) until the acid acts rather freely upon them; rough cast iron requires a stronger liquid than smooth wrought iron. After being again washed in water, they are "scratched" at the brush (§ 80), and if they are very coarse castings or rusty articles, they may require several soakings in the dilute acid, and scourings with sand and a hard brush, and even filing to make them quite clean.

173. *Copper, Brass, and German Silver.*—Those formed of copper, brass, or German silver should be boiled in the potash liquid, washed in water, dipped into nitric acid or into "dipping liquid" (§ 82), and then washed in water, and dipped into a solution of nitrate or cyanide of mercury (§ 84) before immersing them in the silvering solution.

174. Sometimes, in order to assist in cleaning the articles, they are suspended for a short time in the depositing liquid, in contact with the positive pole of the battery, unless they are very foul, or the solution is too valuable; this dissolves the surface, and loosens the impurities. In every case they should be well rinsed with water to remove the adhering acid, before dipping them into the mercury solution, or immersing them in the depositing vat. All objects which are to have a definite weight of metal deposited upon them are weighed, and their weight noted down after they have been cleaned ready for "quicking" with the mercury.

175. *Wiring Articles.*—The articles, having been cleaned thoroughly, have wires of copper attached to them, to suspend them by when in the vat. The wires differ in size with different articles: with small ones, such as spoons, knives, forks, snuffers, teapots, jugs, and such articles, size No. 20 or 22 of the Birmingham brass wire gauge, and about 18 or 20 inches long, are used. Very large articles, such as fire-irons, fenders, hat-stands, and articles of ornamental iron-work, are suspended in the solution by strong copper or brass hooks; in some cases where a very safe connection is required, the wires are soldered to the articles.

176. *Preparing Articles for Adhesive Deposits.*—We have already explained how necessary it is that all articles intended for the depositing vat should be cleaned in the most perfect manner possible before being immersed in the depositing liquid, otherwise the deposit will not adhere, and in consequence of the perfect degree of cleanliness required, the cleaning often involves more trouble than the depositing. Articles of copper, brass, or German silver, which are to *be silver-plated,* should be dipped into one of the solutions of mercury

(§ 84), and *the least film* of mercury put upon them; otherwise the deposit will either not adhere at all or will be unsound. They should also be plunged while still wet from the above processes into the depositing vat. The practical minutiæ of preparing the surfaces of different metals for receiving adhesive deposits of other metals varies in almost every manufactory, and much information yet remains to be developed upon this point; for want of this knowledge the most skilful operators sometimes fail in producing perfect adhesion, especially upon zinc, cast iron, steel, and Britannia metal.

177. *Preparing Metals for Non-adhesive Deposits.*—Metal articles which are to receive non-adhesive deposits, such as medallions, of which copies are desired in copper, should be allowed to remain a sufficient time to slightly oxidise after being cleaned, before being plunged in the depositing vat, the oxide preventing adhesion. In some cases they are rubbed over with cotton wool slightly moistened with a very weak solution of bee's wax dissolved in camphine in the proportion of a piece of wax of the size of a small pea in a quarter of a pint of the spirit; others use a little sweet oil, which is immediately wiped off with a fresh piece of dry cotton wool.

178. *"Stopping-off" to Prevent Deposition.*—Many articles which are to receive deposits require to have portions of their surface "stopped-off," to prevent the deposit spreading over those parts; for instance, in taking a copy of one side of a metal medallion, the opposite side must be coated with some kind of varnish, wax or fat, to prevent deposition; or in gilding the inside of a cream jug which has been silvered on the outside, varnish must be applied all round the edge on the outside for the same reason. For gilding and other hot solutions, copal varnish is generally used; but for cold liquids and common work, an ordinary varnish, such as engravers use for a similar purpose, will do very well. In the absence of other substances a coating of sealing-wax dissolved in naphtha will answer every purpose. The coating of varnish must be allowed to dry.

179. **Moulding and Copying Works of Art.**—The electro-depositor who includes in his business the multiplication of works of art, as well as the simple plating of metal articles, will require a knowledge of the art of moulding. To copy both sides of a metallic coin or medal in the mixture of gutta-percha and marine glue recommended (§ 85), take a strip of thin sheet copper, brass, or tinned iron, about an inch wide, wind it closely round the edge of the medal, and solder its ends together; wipe the medal and take two balls of the composition, quite hot and soft, and press them simultaneously against the faces of the medal, working the material from the centre towards the circumference to exclude bubbles of air; place two thick plates of cold metal, one on each side, and gradually screw up the whole in a vice,

or screw press, gently at first, but increasing the pressure to a high degree as the materials become hard. When it is quite cold, which will be in about two hours, the copies may be easily removed from the original, by inserting the end of a gimlet in their backs, and drawing them out; they are easily removed, because the composition slightly contracts in cooling. They will present fine impressions of the original, and be perfectly free from air bubbles if the operation has been carefully performed. For large articles a powerful press is employed.

180. *Elastic Moulding.*—If the medallion is undercut, it must be copied in "elastic moulding" (§ 86), thus:—Encircle its edge by a strip of stout paper, and pour the mixture, quite hot, and of the consistency of treacle, upon its surface to the depth of half an inch or more, according to the size of the medal and the depth of its hollow parts, brushing its surface beneath the liquid with a brush having fine and long hairs, to remove air bubbles. Allow the mixture to remain until it is quite firm, which will be from 2 to 24 hours, according to its bulk; take off the paper, and remove the mould very gently, carefully stretching and drawing it at the same time in the direction of the overhanging parts, to prevent injury. Should the object to be copied be a hollow metallic bust, proceed as follows:—Partly fill it with sand, to make it heavy and thus prevent its rising in the liquid, and cover its opening by sticking a piece of millboard strongly over it; then suspend the bust in the centre of a cylindrical and taper vessel, a few inches deeper and wider than itself, and pour the melted composition in steadily, until it is a few inches above the top of the head, tapping the bust, and inclining the outer vessel, to facilitate the escape of air bubbles. When the composition is quite firm, which it will be in about 20 hours, it may easily be removed from the vessel by shaking, if the vessel has been previously well oiled; the mould may then be removed from the bust by previously marking on its lower end the position of the face, passing a knife carefully up the back of the bust nearly to the crown of the head, and opening the elastic mould with your hands, whilst a second person lifts out the bust. If the original bust is composed of plaster, it must be previously saturated with oil to prevent the melted composition adhering to it.

181. **Rendering Moulds Conductible.**—To render the surfaces of non-metallic moulds conductible, there are two methods in use.—1st. To cover them with a thin film of blacklead by brushing; and—2nd. To coat them with a minute film of gold or silver by chemical means. The first of these methods is generally used for moulds composed of gutta-percha, wax, resinous composition, or plaster saturated with oil, where the parts are not much undercut; and the second for elastic moulds, because the blacklead cannot be readily applied to all their *recesses*.

182. *Blackleading.*—To apply blacklead to a small round or oval medallion formed of gutta-percha, or of gutta-percha and marine glue, first insert the sharp end of a piece of copper wire, size No. 16 or 18, and about 15 or 20 inches long, into the edge of the mould near its face, then pass a piece of fine copper wire, size No. 28 or 30, once tightly round the edge of the mould close to its face, securing its ends to the other wire. Fix a strip of paper about 1 inch wide, by means of sealing-wax, tightly round the edge, to prevent the blacklead passing anywhere except upon the face of the mould. Apply the blacklead by a soft camel's hair brush with a large and thick body of short hairs, breathing upon the face of the mould occasionally to facilitate the adhesion of the blacklead; and when the medal is perfectly black and bright, blow off the superfluous powder, and remove the paper; it is then ready for receiving a deposit, the whole operation occupying about 10 or 15 minutes with a small object the first time of preparing it, but less in subsequent operations. If the mould is very large, and especially if it has deep hollows in its surface, it will require, after being blackleaded, to have several short and fine copper "guiding wires" carefully attached to the main wire, and their free ends slightly inserted in the face of the mould in the most hollow and distant parts, or to lie in contact with them, in order to cause the deposit to commence and spread there as well as round the edge. If this precaution is not taken, the deposit will be much thinner over those parts than upon the nearer and more prominent places, and sometimes will not spread over them at all.

183. *Preparing the Surfaces of Elastic Moulds.*—Elastic moulds are treated in a different manner. 1st. A stout connecting wire is attached, then a number of fine copper "guiding wires" are twisted round it, and their free ends slightly inserted in the face of the mould in all the hollow and distant parts; the mould is then either dipped into the phosphorus solution (§ 87), or its surface is covered with that liquid; and, after it has been drained clean, it is allowed to remain until perfectly dry; the silver solution (§ 87) is next applied to it, in like manner, for several minutes, until it appears black, with a metallic lustre like black china; it is then gently rinsed with distilled water, and the gold solution (§ 87) applied in the same way, which gives it a yellowish aspect; after another rinsing in distilled water it is ready for receiving a deposit. Elastic moulds are also prepared by brushing them over with the finest quality of copper bronze—that used for printing purposes is suitable.

184. *Moulding by Phosphorus Composition.*—Some objects which are not much undercut are moulded in the phosphorus composition (§ 87); and, in some cases, where they are undercut, as well as busts, they are first copied in the elastic moulding, and the elastic mould re-

copied in this material, the composition being but barely melted that it may not dissolve the elastic moulding. In either case, instead of immersing the mould into the phosphorus, silver, and gold solutions, it is only immersed in the two latter, the phosphorus contained in the mould itself serving to reduce the silver and gold.

185. *Preparing Surfaces of Glass for Deposition.*—Glass surfaces may be prepared for receiving a deposit by means of the phosphorus, silver and gold solutions, but not very satisfactorily. A better method, which has been tried, is by silvering them by Drayton's patent process, thus:—Take 1 part, by weight, of liquid ammonia, 3 parts of alcohol, 2 parts of nitrate of silver, and 3 parts of distilled water; dissolve the silver salt in the water, add the liquid ammonia and the alcohol, shake the mixture, allow it to remain until quite clear, and pour off the clear part into the glass vessel to be silvered, which must be perfectly clean; then add to it 1 quarter of a part of grape-sugar dissolved in weak spirits of wine, mix the liquid, and heat it to about 150° or 160° Fah. for about 20 or 30 minutes, and the glass vessel will become silvered; the liquid may then be removed, the vessel gently rinsed with distilled water, a connection formed by means of a fine copper wire with the film of silver and the battery, the vessel filled with a suitable depositing liquid, an anode immersed, and the surface deposited upon in the ordinary way. If the process has been successfully performed, the deposit, whether of silver or copper, spreads instantaneously over the silvered surface. The only way by which we have been able to form an adhesive deposit upon glass or porcelain has been to send the article to a glass and porcelain gilder, and have gold leaf burnt into their surfaces, and then depositing upon them in the usual manner.

186. *Immersion of Articles in the Vat.*—The operator having prepared the various articles and moulds, will immerse them in the depositing solution, having previously immersed the anode and completed all the connections, taking care always to connect the article to receive the deposit with the zinc of the battery, and the metal to be dissolved with the copper or silver.

187. **Regulation of Battery Power.**—In depositing all metals, it is of the greatest importance that the battery power be properly regulated, and this may be done in a variety of ways, which collectively consist, either in making alterations in the battery, in the depositing vessel, or in the wires connecting them. The E.M.F. of the current is increased by increasing the number of alternations of the battery plates; by increasing the conductibility of the battery liquid or depositing solution, which may be effected either by the addition of free acid to the battery or more salt to the solution; or by increasing the thickness and decreasing the length of the con-

necting wires. The *quantity* or *strength* of the current is increased by immersing all the battery plates deeper in their liquids, also by those means which increase the E.M.F. The "strength" of current from a dynamo-electric machine is usually regulated by interposing a greater or less length of sufficiently thin wire of iron, German silver, or platinum, in the circuit. Both the E.M.F. and the quantity may be decreased by separating the electrodes in the depositing vessel farther asunder, or by interposing a long and fine iron wire in the circuit. The most usual means adopted of increasing the electro-motive force of the current is to add to the number of the batteries; and for increasing the *quantity*, to immerse all the battery plates deeper in their liquids. Sometimes, to increase the power, the temperature of the liquid may be raised, or the article placed nearer the dissolving metal; and, when a smaller quantity of current is required than the ordinary batteries can conveniently supply, a piece of sheet metal may be hung in the depositing solution with the receiving article, to receive a portion of the deposit, and thus transfer some of the power from the article to itself.

Since the publication of the first edition of this book, current electricity on a large scale has been produced by means of dynamo-electric machines, at a very much lower cost than by voltaic batteries, and the currents from those machines have been extensively applied in purifying crude copper. Mr. James Elkington was the first person who did this commercially, and patented the process. The process is now worked on a large scale by the North Dutch Refining Company at Hamburg; Messrs. Oeschger and Mesdach, at Biache; M. Hilarion Roux, at Marseilles; The Oker Foundry Company, in Saxony; Messrs. Lyon-Allemand, at Paris; Messrs. Elliott and Company, at Swansea; M. Andre, at Frankfort-on-the-Maine; at the Mines of Mansfield, in Prussia; and at other places. The first of these companies is said to deposit 2½ tons daily by the aid of those machines. In this process, large thick slabs of the crude reduced metal are used as anodes placed vertically in large vats containing an acidified solution of blue vitriol, and the deposit is received upon thin sheets of pure copper placed opposite them as cathodes in the vats. Nearly all the impurities, being insoluble in the liquid, fall from the anodes, and settle in the state of mud at the bottom. The sediment consists of a large number of substances, and includes gold and silver, which are subsequently extracted. The soluble impurities, consisting chiefly of iron, are not deposited, and when they have largely accumulated they are separated by chemical means, and the vats charged with fresh solution.

188. *Electro-motive Force and Quantity of the Current.*—The E.M.F.

of the current obtained from a series of batteries depends upon the *number of alternations* of the metals, whilst its *quantity* depends upon the *amount of immersed surface in each alternation*, and it makes no difference whether that amount of surface is in one battery plate or in many or in one or many containing vessels. A series of similar batteries may be so connected together by wires or other conductors, as to give

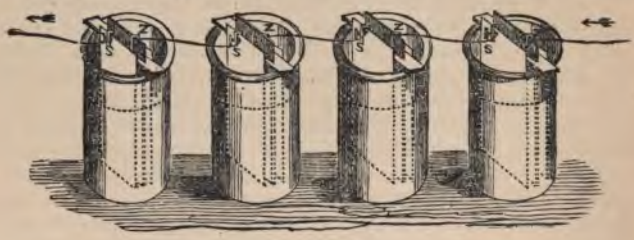

FIG. 32.

either E.M.F. or quantity of current, provided they have screws or other conveniences for attaching the wires to the plates. For instance—1st, if we have 4 pairs of plates, in 4 separate cells, and connect them alternately, thus (Fig. 32), zinc, silver—zinc, silver—zinc, silver—zinc, silver, by wires from the terminal plates, we obtain a current possessing the E.M.F., of 4 pairs, and the quantity

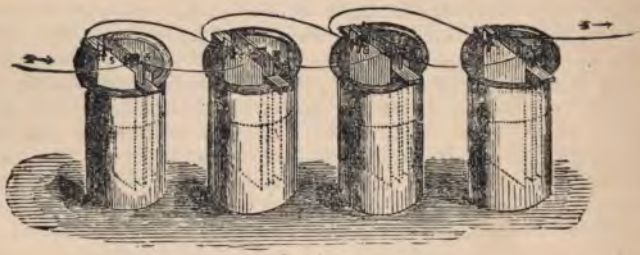

FIG. 33.

of 1; but if, 2nd, they are connected, all the zincs by 1 wire, and all the silvers by another wire (Fig. 33), with 1 portion of each wire left convenient for making connections, we obtain a current possessing the quantity of 4 pairs, and the E.M.F. of 1; and, 3rd, if they are arranged in 2 series or rows, 2 pairs in each, each series being connected alternate fashion, the end silvers of each row facing one way

and connected by 1 wire, and the terminal zincs facing the opposite way and connected by another wire, and these wires left free for connection with the vat (Fig. 34), we obtain a current possessing the E.M.F. of 2 pairs and the quantity of 2. By contrivances of connection like these, any number of batteries, provided they are similar in kind, charged alike, and have suitable connecting screws attached, may be connected together so as to give any desired quantity, or E.M.F. of current within the limits of their power; thus, a battery of 100 pairs may be arranged to yield a current having the E.M.F. of 100 pairs, and the quantity of 1; the quantity of 100, and the E.M.F. of 1; the E.M.F. of 50, and the quantity of 50; or any intermediate degree of each.

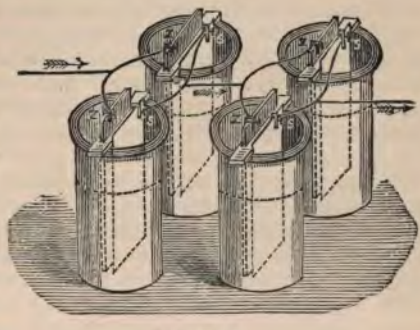

FIG. 34.

189. **Regulating the Quantity of Deposited Metal.**—The quantity of metal dissolved and deposited in the vat is in direct proportion to the quantity of zinc dissolved and acid consumed in each alternation of the battery. With a perfect depositing liquid, good battery arrangements, and pure materials, for every equivalent of zinc dissolved in each alternation of the battery an equivalent of metal is dissolved on one side, and an equivalent set free on the other, in the depositing vessel. For instance, for every equivalent (65· parts) of zinc so dissolved, and 98· parts, or 1 equivalent of oil of vitriol consumed in the battery, an equivalent (63·5 parts) of copper is deposited in the sulphate of copper solution, or an equivalent (216· parts) of silver in the cyanide silver plating liquid, and similar quantities of copper or silver dissolved at the anode. But in practical working the materials are rarely or ever pure, or the arrangements perfect; the zinc nearly always contains a small proportion of other substances, the mercury contains tin or lead, and the sulphuric acid contains a little nitric acid. The acid liquid of the battery is often too strong; much acid liquid is frequently wasted, being thrown away before it is completely exhausted. The zinc plates have not been kept amalgamated, or the silver well platinized, or the plates have been suffered to remain too long in the liquid when not in use. The metal of the anode also is frequently impure; occasion-

ally some of the deposit is allowed to redissolve, in consequence of the battery power becoming low, and from not stirring the liquid; in some solutions, a part of the battery strength is expended in evolving gas at the cathode; and, finally, the repeated operation of "scratching" removes some of the deposit. Allowing for all these and other unavoidable sources of loss in practical working, about 1 pound only of copper can be deposited in the ordinary sulphate solution, by the consumption of from 1¼ to 1½ pounds of zinc and an equivalent quantity of acid, in each alternation of the battery. To increase the quantity of metal deposited in a given period of time, the battery plates should be sunk deeper in their liquids, and the resistance in the circuit diminished.

190. *Regulation of the Quality of the Deposit.*—The quality of the deposited metal, *i.e.*, its degree of cohesion, hardness, flexibility, &c., depends upon the strength of the current. As a general rule, the greater the E.M.F. and the smaller the quantity of the current, the harder and brighter is the deposited metal; and the greater the quantity and the smaller the E.M.F., the less coherent and the softer it is. To obtain a very hard, bright, and crystalline deposit, we should use a current of small quantity and high E.M.F.; and to obtain a soft black powder deposit, we should employ large quantity and low E.M.F.; the combination of moderate quantity and moderate E.M.F. produces a coherent reguline deposit, possessing the ordinary characteristics of the particular metal. These results can only be obtained with a good depositing liquid, and with metals, such as copper, silver, gold, &c., which are known to deposit in a tough reguline state, and not with those—such as bismuth or antimony, crystalline metals—which are not known to deposit in that state.

191. If we are producing a reguline coating, with a 1-pair battery, in a good depositing liquid, with electrodes of the same size as the immersed portion of the battery plates, and it is wished to change the deposit to a soft black powder, the plates of the battery must be immersed very much deeper in the liquid, and a very much larger dissolving plate used in the vat; and if we wish to change the deposit to a crystalline one, several more pairs of batteries should be put on, connect them series fashion, immerse the plates an exceedingly small depth in their liquids, and use a very small anode. These results have a direct reference to the size of the receiving surface; for if, with any given battery and anode, we are producing a black powder deposit upon a very small article, a larger article would receive a reguline deposit, and a much larger one would receive a deposit bordering upon crystalline. Thus it will be perceived that the black powder deposit is a result of too rapid action, and the crystalline one of very slow action.

192. *Spread of Deposit.*—If we wish to make a metal spread rapidly

over a metal of inferior conductibility, such as a long iron rod, we must use a current of high E.M.F. and rather small quantity; this will drive it over the surface without causing it to become soft or non-coherent. The action of such a current appears to consist in conferring upon the particles a kind of polarity, a power of grouping themselves into separate warty nodules or crystals, each of which, as it becomes larger, appears to powerfully repel its neighbour, and thus causes the metal to spread rapidly; when this action is continued to a considerable thickness of deposit, especially in cold weather, the metal is exceedingly hard and easily broken into a number of distinct grains or nodules, which are in the form of warty lumps with rounded edges when the action has been rather too quick, or the liquid not sufficiently cold, and composed of more or less perfect crystals, with edges sometimes beautifully defined, when the action has been very slow, and the liquid very cold and undisturbed. With the E.M.F. of 100 pairs of Smee batteries, acting for a long period of time in cold weather, and the quantity of the current kept down to the lowest possible degree, we have seen a tough deposit of zinc spread over several square inches of clean gutta-percha; and in depositing copper with a current of rather high E.M.F. and small quantity, upon blackleaded gutta-percha medallions, we have repeatedly observed, that where there was a sunk boundary line near the edge, the deposit remained quite thin, as if powerfully repelled, whilst on each side of the line it was very thick, and on the outside edge, accumulated in large warty masses, hard and distinctly separate, and containing as much metal as the whole of the medallion besides.

193. **Management of Batteries.**—The most suitable strength of liquid for filling the battery cells consists of 1 measure of sulphuric acid and about 20 measures of water; a stronger liquid may be used, even to 1 part of acid to 10 or 12 parts of water, but then the zinc plates require constant watching and frequent amalgamating, to prevent waste. If the acid liquid is very strong and the electric action energetic, the zinc plates will require to be examined every day, to see that there is no local action, *i.e.*, chemical action in particular places; and when gas is found to be freely rising from them, as well as from the silver or copper, or when any dull patches appear where the acid has acted too strongly upon them, they should be taken out and amalgamated. They should be frequently amalgamated when new, and afterwards, if much worked, they should be amalgamated every few days; when they become old they should be rarely amalgamated, because it very much weakens the power. When they become so thin as to fall to pieces on handling, new ones should be substituted, and the old ones should either be melted at as low a degree of heat as possible, to prevent loss of mercury, and cast into rods for Daniell's batteries, or

be broken up, put in an iron retort, and the mercury distilled from them at a strong red heat into a vessel of water.

194. The zinc plates should be taken out of the liquid every evening, unless deposition is required to continue all night. After the battery has been at work a few days, a little more acid should be added, and the liquid stirred; and this should be done as often as the power gets low, until at length the liquid becomes thick and nearly saturated with zinc salt, and the salt crystallizes about the edges of the cells; it is then time to throw it away and put fresh, or it may be filtered, evaporated, and crytallized, and the resulting salt (sulphate of zinc) preserved for depositing purposes. If any of the silver or copper plates of the batteries become covered with a deposit of zinc whilst working, it shows that all the acid in that cell is exhausted, and that more should be added, or fresh liquid put in. This only happens in a Smee's battery, or in the old zinc and copper battery. The deposit of zinc may be easily and quickly removed by the addition of acid to that cell, by a fresh liquid, or by immersing the coated plate in dilute sulphuric acid as long as gas is evolved from it.

195. If copper plates are used in the batteries, they should be heated red hot all over every week or ten days, and quenched in water, and then dipped in "dipping liquid" (§ 82), or in nitric acid; and if platinized silver plates are used, they should be re-platinized as often as they become light in colour, or their power becomes low, which will happen once in 2 or 3 months with constant working. The re-platinizing greatly increases the power of the battery. Great care must be taken that the zinc plates never touch the silver or copper ones when wet, otherwise the mercury will get upon the latter, and much weaken the battery power; and with the silver plates cause them to drop to pieces if they are very thin.

196. *General Rules for Working Solutions.*—In working any depositing liquid—1st, avoid doing anything which will alter the chemical composition of the liquid, or even the proportions of its ingredients, except the water—that may be altered in proportion in most liquids without much inconvenience; 2nd, adapt your electric power to the liquid, rather than the liquid to the power, and regulate the deposit rather by alterations in the battery than by alterations in the depositing vessel, except as regards the distances of the electrodes or the temperature of the liquid—these may be altered with safety, and sometimes with convenience; and, 3rd, as a general rule, let your dissolving metal expose a larger immersed surface than the receiving article.

197. *Position of Articles and Dissolving Plates.*—The best practical position for the dissolving plate is the vertical, the dissolving plate and the receiving article being suspended in the liquid facing each other, the latter being rather the lowest of the two, and both wholly immersed.

The horizontal position, with the dissolving metal above, although the most philosophical arrangement, does not succeed in practical working, because the metal used for dissolving is never quite pure (with copper, especially), and the impurities from it fall upon the surface of the receiving article beneath, and make it rough; in addition to this, the position of the article prevents our being able to examine it easily or remove it conveniently. If the article to be coated has a very irregular outline, either the dissolving plate should be bent somewhat to its form, so that the two may be nearly equi-distant at all parts; or the article should be often shifted in its position, so as to produce a nearly uniform thickness of deposit all over. The nearer the receiving article is to the dissolving plate, the more rapid is the deposit, and a large body of liquid deposits more rapidly and more evenly than a small one; large connecting wires are more favourable to quick deposits than small ones. The greatest thickness of deposit always takes place upon the most prominent places, *i.e.*, upon those parts nearest the dissolving metal.

198. *Motion of the Articles in Vat.*—In some solutions—for instance, the double sulphite of silver and potash—if the current is too strong to produce a good deposit, motion of the articles will prevent the deposit becoming bad. In some plating establishments, the articles in the vats are kept in constant motion, gently swinging to and fro, the metal frame upon which they are suspended having 4 small wheels running upon 4 small inclined planes fixed upon the edges of the vat, and kept in constant motion by steam or other available power.

199. *Temperature of Solution.*—Several solutions, such as the cyanide of copper and potassium, the cyanide of gold and potassium, &c., require to be kept hot, in order to make them conduct freely, and yield suitable metal; not that they cannot be worked cold, but that they work much better and quicker hot, which more than compensates for the expense of heating them.

200. *Protection of Depositing Liquids from Light.*—Some liquids, such as the double sulphite of silver and potash and the hyposulphite of silver and potash, require to be protected as much as possible from the influence of light; and even the ordinary cyanide silver liquid is better screened from an excess of this agent.

201. *Clean Connections Necessary.*—In every case we must be very careful to observe that the circuit is complete, and that it is capable of conducting the current freely throughout; that the articles to be coated are conductors of electricity; and that their surfaces, as well as all the ends of the wires at their various points of contact are perfectly clean.

202. *Management of Coppering Liquids.*—With the sulphate of copper solution (§ 120) no particular management is required, beyond

the general rules already laid down (§ 196). It is not suitable for depositing direct upon zinc, tin, lead, iron, or steel. Articles formed of these metals are first coated with a thin layer of copper in the cyanide of copper and potassium solution (§ 120), then well washed, and transferred immediately to the sulphate solution, and the remainder of the required thickness of copper deposited.

203. **Uses of Copper Deposition.**—Among the many uses to which the electro-deposition of copper has been applied, we may mention the following:—To make copper cells for Daniell's batteries; making copies of stereotype plates, engraved copper plates, and engraved rollers; coppering the surface of printing type; coppering steel pens; to protect iron and steel goods from rusting, coating telegraph wires, ship's bolts, screws, &c.; to make copies of Daguerreotype pictures; to make coppered cloth; to coat glass chemical vessels; to coat and protect metal and plaster statues, busts, and sculptured works; to preserve the form of flowers, fruits, ferns, sea-weed, insects, reptiles, &c.; to make medallions, busts, and various figures and ornaments in copper; it has also been applied in the arts of glyphography and electro-tint printing; and largely in purifying crude copper.

204. *Making Objects in Copper, Coppering, &c.*—To make a cell of Daniell's battery in copper, coat the inside of a glass jar or earthern jelly pot with wax, resin, or stearine, by making the vessel hot, then either blacklead it thoroughly, or treat it with the phosphorus, silver, and gold solutions; or, what is more simple, coat it uniformly all over the inside with the phosphorus moulding composition (§ 87), and then treat it with the gold and silver liquids. Make a connection by a fine copper wire with the lower part of the coating, fill the vessel nearly full of the sulphate of copper depositing solution (§ 120), suspend in it a sheet of copper, and connect the sheet of copper and the fine copper wire with a small battery of 1 or 2 pairs. If, instead of the battery process, we adopt the single cell arrangement, containing dilute sulphuric acid and a piece of zinc, placing a porous cell in the sulphate solution, and connecting the fine copper wire with the piece of zinc; in either case a deposit of copper will soon spread over the entire inside surface of the jar, especially if it has been prepared by the phosphorus method. Engraved steel plates are copied by stopping-off the back with copal varnish, allowing the plate to become perfectly dry, immersing it in the cyanide coppering liquid, and depositing a thin film of copper upon it, then washing it well and at once immersing it in the sulphate of copper solution, and depositing the required thickness of copper upon it; this will require from 24 to 48 hours. The surface of the steel should be previously prepared for a non-adhesive deposit, otherwise the two metals cannot be separated.

205. *Copying Wood-cuts in Copper.*—For printing purposes, where a

large number of impressions of a particular wood-cut is required, the plan of taking copies of the engraved wooden block in copper by the electro process, and using those copies instead of the original block to print from, has been gradually extending itself for many years, and has now attained a considerable degree of importance. To copy an engraved wooden block, the engraved surface is first moistened with water, and firmly enclosed by a shallow frame; a thick piece of gutta-percha, more than sufficient to fill the enclosed space, and made quite soft by heat, is then laid upon it, commencing its contact at the centre of the engraving and proceeding outwards, so as to exclude all air-bubbles; a plate of cold iron is then laid upon the gutta-percha, and the whole subjected to pressure, gentle at first, but increased to a high degree as the substance cools. The block and copy are then separated, and the figured surface of the gutta-percha (with connecting and guiding wires previously attached) is treated in the usual manner with blacklead or with the phosphorus, silver, and gold solutions; copper is then deposited upon it in a solution of sulphate of copper, until a moderate thickness of deposit is obtained, which will occupy at least 12 or 18 hours; when sufficiently thick the deposit is removed, its back made rigid by a layer of solder or type-metal (the surface being previously moistened with a solution of chloride of zinc to make the solder adhere), the back is planed flat, and mounted upon a block of wood to the height of the type. In London this process is carried on upon a large scale, some of the copies being upwards of 2 feet square. Engravings upon steel are copied in an exactly similar manner to those upon wood.

We have recently tried some experiments with a view of making the deposit of copper upon gutta-percha and marine glue spread more rapidly than it does by preparing the surface with blacklead, it being a matter of some importance in copying wood-engravings for periodicals of such large circulation as the *Illustrated News* that the time occupied in copying them be reduced. Our experiments have resulted in some success, and we give the following results of them for the benefit of the printing trade.

After having formed a reverse copy in gutta-percha and marine glue of the engraved wooden block, and affixed the conducting wires to it, take a mixture of 1 measure of spirit varnish, and either 4 or 5 measures of vegetable naphtha, and apply it very sparingly in a thin layer by a soft camel's-hair brush over the whole surface of the mould where the deposit is desired to be spread. Whilst the surface is still wet, cover it with a mixture of 3 parts of yellow and 1 part of white bronze powder, and bring the powder in thorough contact with the whole of the moistened surface by striking it all over with a dry, soft brush; then gently brush off all the superfluous powder. The bronzed

mould may now be immersed in the ordinary sulphate of copper solution, and the following actions will occur:—The particles of white bronze powder being composed almost wholly of tin, and those of yellow bronze containing much copper, those of tin will dissolve and coat themselves with copper by simple immersion process (§ 4), and those of brass or copper (the yellow ones) will become coated by their contact with those of tin (Two Metals and One Liquid Process, § 7), and thus a thin deposit of copper will almost instantaneously spread all over the bronzed surface. This effect will, of course, take place without connecting the mould with the battery, but they may be immediately connected together, and a deposit will spread almost instantaneously over the whole of the bronzed surface by the ordinary battery process, through the medium of the bronze and the thin deposit already mentioned, and may be continued to any required thickness in the usual way. In our earlier experiments with this method, yellow bronze alone was used, which did not reduce the copper by simple immersion; but even then medallions were repeatedly covered with a deposit of copper in from 2 to 5 minutes, which would occupy from 20 to 45 minutes when prepared by blacklead in the usual manner. The addition of white or tin bronze causes the deposit to spread as rapidly as when the surface is prepared by the phosphorus solution, but without the disadvantage, which occurs in using the latter, of making the deposited metal brittle. The effect of using white bronze alone was not so satisfactory.

The surface of the copper copy so obtained is bright and clean, and the character of the deposited metal is good, but the surface obtained is hardly so smooth and fine as that obtained with blacklead; the difference, however, is very slight, and it is sufficiently smooth for all ordinary purposes, and for the object sought, if care be taken to blow off or otherwise remove all superfluous bronze powder before immersing the mould in the vat. We hope that those who have the opportunity will try it upon a larger scale.

206. *Copying Set-up Type in Copper.*—The process of electrotyping has also been gradually encroaching upon that of stereotyping, and has, we are informed, almost superseded that process in America. The plan adopted is similar to that of copying woodcuts, viz., to lay a sheet of softened gutta-percha upon the surface of the page of type, and subject it to increasing pressure until it is cold; the gutta-percha copy is then removed, and treated as in copying wood engravings. It would be advisable to try a somewhat softer material for this purpose, such as the mixture of gutta-percha and marine glue which we have recommended (§ 85). This material takes a sharper and smoother impression than gutta-percha alone, and the deposit spreads over it *more rapidly*; and, being softer, it would enter more freely and with

less pressure between the fine lines of the letters, and still not be sufficiently soft to enter the minute crevices between the body of the types. If a solution of grape-sugar (as used in Drayton's patent process for silvering glass), aldehyde, or other reducing agent, was substituted for the phosphorus solution, for reducing the silver upon the surface of the mould, it would be an advantage, as besides the dangerous character of the phosphorus, it has an offensive odour, and the copper deposited upon surfaces prepared by it, is moreover, invariably brittle.

The mould may also be prepared for a deposit by blackleading; it will require a first-rate quality of blacklead, and prolonged and attentive brushing, but will then afford a good result. The air-bubbles may be removed when the mould is in the liquid, by directing a powerful upward current of the liquid against them by means of a vulcanized india-rubber bladder, with a long-curved glass tube with a fine orifice (Fig. 35) attached to it; taking care not to raise any sediment.

Fig. 35.

The advantages of electrotyping over stereotyping are numerous; the metal is harder, takes a sharper impression of the mould, and delivers the ink much more readily than type metal, besides being a cleaner process; it also takes up less ink, and consequently the printed pages dry more quickly. Both woodcuts and letterpress have also been copied in plaster of Paris, and the deposit of copper formed upon that; but this material is much inferior to gutta-percha for the process. Messrs. Bradbury and Evans were long extremely successful manipulators in this branch of electrodeposition, and their apparatus is the most perfect of its kind. In this establishment the temperature of the room is carefully attended to, and the vessels containing the solutions have glass covers. The result of this careful manipulation has been that, in some instances, successful deposits of large *Illustrated News* engravings have been formed and taken off in eight hours; this can only have been effected by the most perfect blackleading, keeping the solution in excellent condition, and working with the maximum of battery power. Gutta-percha and marine glue is well worthy of a trial, and the use of bitumen with gutta-percha is also a good idea; the marine glue would be better, because it is tougher.

Iron and steel wire may be coated with an adhesive deposit of copper, by first coating them, with their surfaces perfectly clean, in the cyanide coppering liquid, and completing the deposit in the ordinary sulphate solution. The coils should be kept separate from each other in the liquid by suspending them upon a horizontal brass

rod, turning it occasionally to cause a uniform deposit. Iron screws and nails may be treated in a similar manner except that they should be contained in a wicker basket, and shaken occasionally to produce a uniform deposit.

207. *Copying Daguerreotype Pictures in Copper.*—The most interesting and beautiful application of the deposition of copper, and at the same time one of the easiest to be effected, is that of copying Daguerreotype pictures. First solder a wire to the back of a plate near the edge; varnish the back and edges, and allow it to dry; hang it in a clean sulphate of copper solution, which is perfectly free from dust or grease on its surface; and, in the course of 20 or 30 hours, if about 2 pairs of small Smee batteries have been used, the deposit will be sufficiently thick to be removed; it should then be taken out, well washed, wiped perfectly dry, and a narrow strip be cut off its edges with a strong pair of scissors; the two may then be easily separated by inserting the point of a knife, or the end of a thin wedge of hard wood, between them at the edges. If the process has been carefully managed, and the original picture is a strong one, a most beautiful and vivid copy will be obtained; and if the picture is not only a strong one, but has also been well fixed by Fizeau's process, a number of successive copies may be taken from it, but their intensity, as well as that of the original, appears to diminish in each succeeding trial. With a vivid original picture, clear solution, very regular and undisturbed action of the battery, and a fine deposit, we have observed a most strange phenomena, viz., the picture has not entirely disappeared, even in 20 hours, although the coating of copper has constantly increased in thickness; the image has penetrated quite through the deposited metal and appeared upon the back, even upon deposits as thick as an address card. In some cases the figure was optically positive, and in others negative.

208. *Coating Plaster Models, Flowers, and Clay Figures with Copper.*—Busts and other similar objects may be coated by saturating them with linseed oil, then well blackleading, or treating them with the phosphorus, silver. and gold solutions, attaching a number of guiding wires, connected with all the most hollow and distant parts, and then immersing the object in a sulphate of copper solution containing no free acid, and causing just sufficient copper to be deposited upon them by the battery process to protect them, but not to obliterate the fine lines or features. Flowers, fruits, ferns, sea-weed, insects, &c., may be prepared by the phosphorus, silver, and gold liquids, and the copper deposited upon them, either by the single cell or battery process, in a neutral sulphate of copper solution.

209. *Coppering Cloth.*—To copper cloth, first stretch it upon a sheet of copper slightly curved, so that it may be in close contact with the

metal all over; then varnish the back or hollow side of the copper, and deposit on the opposite side, by the battery process, from a sulphate solution not containing much free acid, until the meshes of the cloth are quite filled with copper, and the metal and cloth firmly united together; the deposit may then be removed and well washed; the original sheet of copper should, of course, be properly prepared for a non-adhesive deposit. By Mr. J. Schottlaender's process the cloth is passed under either a plain or an engraved copper roller, horizontally immersed in a sulphate of copper solution not containing much free acid, and a deposit takes place upon the roller as it slowly revolves. The meshes of the cloth are thus filled with metal, and the design of the roller copied upon it, the coppered cloth slowly rolled off, and passed through a second and closely contiguous vessel filled with clean water. The roller is properly prepared for a non-adhesive deposit.

210. *Etching Copper.*—In etching a copper plate by electricity, first solder a wire on the back, then varnish the back, and cover the front with a thin layer of engravers' etching ground; draw the design upon the front surface with an etching needle, cutting through this material to the clean surface of the copper. Having completed the etching, hang the plate as an anode in the ordinary sulphate of copper solution, opposite a suitable cathode of brass or copper. The current of electricity in passing out of the engraved lines into the liquid causes the copper in them to dissolve, and thus etches the design in the plate. The different gradations of light and shade are produced by suspending cathodes of different forms and sizes opposite the plate to be etched, in different positions and at different distances from it, thus causing the etching to be of different depths in different parts, the deepest action being always at the parts of the electrodes nearest together.

211. *Glyphography.* This art consists in varnishing the back of a flat and smooth copper plate, laying first a thin coating of white etching ground upon its front side, and then a layer of black etching ground upon that, engraving the design upon the coating with different engraving tools, then blackleading the whole of the engraved surface, and depositing a thick sheet of copper upon it in a sulphate solution by the battery process; the deposited plate is then removed, its defects corrected, and fixed upon a block of wood in the same manner as a stereotype plate, ready for printing by the ordinary hand-press.

212. **Management of Silver Solutions.**—Silver plating liquids require much more care and attention than the sulphate of copper solution. Articles formed of zinc, iron, or steel, require to be coated with a thin film of copper in the cyanide of copper liquid, before being immersed in the cyanide of silver solution. Those formed of Britannia metal, tin, or pewter, are taken direct from the hot potash liquid without rinsing in water, and immersed a short time in a cyanide of silver

solution containing considerable supplies of free cyanide, with a large anode, and a current of considerable intensity from a strong battery is passed through for several minutes until the articles receive a thin deposit of silver; they are then transferred to the ordinary vat to receive the full amount of deposit. Those of lead are first scraped or otherwise made quite clean and bright by mechanical means, and then treated in the same manner as those of Britannia metal. Articles of copper, brass, or German silver, after being properly cleansed, are dipped into the solution of nitrate of mercury or of cyanide of mercury and potassium (§ 84), then rinsed in a vessel of water, and immediately suspended in the depositing vat. If they are immersed without this preparation, the deposited silver does not always adhere firmly.

213. **Peculiarities in Practical Silver Deposition.**—Peculiar phenomena often occur in the electro-deposition of silver, not only upon different metals, but also upon the same metals in different forms or in different conditions of surface; for instance, according to statements made to me by electro-platers,

1st. If two perfectly similar pieces of thin sheet brass are taken (except that one is perforated all over with small holes), and both be simultaneously immersed in the same solution to be silvered, and with the same battery power applied to each, the latter, although its amount of surface is reduced by the perforations, will become coated with silver much more slowly than the former.

2nd. If a wire gauze cylinder of a Davy lamp be suspended side by side with a piece of thin tubing of the same metal and of the same dimensions, the latter will become coated much more rapidly than the former.

3rd. If two pieces of the same metal—iron for instance—are immersed to be silvered in the ordinary cyanide solution, or to be coppered in the hot cyanide of copper and potassium liquid, each containing exactly the same amount of surface to be coated, but one being in the form of a thin sheet, and the other in that of a thick plate or solid block of metal, the former will become coated much more rapidly than the latter; an effect probably of difference of temperature.

4th. The edges and points of articles, whilst being plated, exhibit a greater tendency to a crystalline deposit than the flat parts, and this tendency is sometimes manifested in depositing silver upon table-knives and forks. It is the knowledge of these and many other peculiarities of different metals and articles met with in practical working, and of the means of overcoming their attendant difficulties, which constitutes one of the chief differences between the practical operator and the theoretical scientific man.

214. **Management of "Bright Solution."**—A bright solution is much

more difficult to manage than the ordinary silvering liquid; if it is not worked constantly and in a uniform manner, it will lose its power of yielding bright metal. If any one of the articles which are being plated in it is disturbed, or removed from the liquid and replaced, that one will not now receive a bright deposit, and the disturbance of the liquid by removing it will oftentimes cause all the neighbouring articles to lose their brightness. If too much "brightening liquid" (§ 144) is added, the solution will be considerably injured; many silver solutions have been irretrievably damaged in this way. A bright solution requires a battery current of large quantity and E.M.F. to work it, and the dissolving plates in it are generally of a darker colour than those in the ordinary silvering liquid; the silver deposited from it is much harder than that deposited from the ordinary plating solution, and has very much the appearance of fused metal; the bright appearance commences at the upper part of the articles and travels downwards; it soon after commences also at their lower extremities and travels upwards, until the bright portions meet each other. If there are small holes in the surface of the articles, dull streaks appear above them. According to my analysis bright silver contains sulphur.

215. **Adding Cyanide of Potassium to Plating Liquids.**—It is necessary to add a little cyanide of potassium occasionally to every cyanide of silver plating liquid, probably because the solutions absorb carbonic acid from the atmosphere, which converts some of the cyanide of potassium into carbonate of potash, and sets hydrocyanic acid gas free. A further portion of the potassium salt may also be decomposed by some means, with formation and escape of ammonia; the necessity of adding a little fresh cyanide is indicated when the dissolving plate begins to change from its ordinary pure white appearance to a dull yellowish gray colour; it is best added in the evening after plating, just before stirring the solution.

216. If the solution is too strong, *i.e.*, if it contains insufficient water, but has silver and cyanide of potassium in their proper relative proportions, it conducts freely, deposits rapidly, and gives a rich deposit of a fine silky lustre; but it is more difficult to manage than a weaker liquid, especially in hot weather, because, from the less mobility of its particles, it is very apt to settle by working into strata of different densities, its upper part becoming exhausted of silver and full of free cyanide, and its lower part becoming nearly saturated with that metal, and deficient in free cyanide. The consequence of this is, that the upper parts of the dissolving plates waste rapidly, whilst the upper parts of the article receive either very little deposit or one of a bad quality, being grey, brown, or yellowish, sometimes of a lilac hue, and generally in dull streaky vertical lines. All these evils may be mitigated by stirring the solution well every night after having

finished plating, or it may be entirely prevented by diluting the liquid with water to a proper extent, stirring it every evening, and working it uniformly. All silvering and other depositing liquids exhibit this tendency to settle into strata in working, especially if worked rapidly, but the most dilute ones show it in the least degree.

If the solution is deficient in water, and contains a great excess of free cyanide, the foregoing evils are all greatly aggravated. In hot weather it becomes quite unmanageable, and the vapours of ammonia and hydrocyanic acid arising from it are overpowering. In this case, the best way to improve it is to add cyanide of silver and water in sufficient quantities to make it of a good composition, keep it in a cool place, stir it daily, and work it constantly in a uniform and careful manner. New solutions, or old ones which have been injured, often improve by daily stirring, with uniform and judicious working. An excess of cyanide of potassium is indicated when the dissolving plates are very strongly acted upon, and the deposit is at the same time either very sparing or of a bad colour.

If the solution is too weak, *i.e.*, if it contains too much water, it conducts sparingly, deposits slowly, and the deposit has a dead white appearance. This may be easily remedied by adding cyanide of silver and cyanide of potassium to it in proper proportions, and working it uniformly a few days with daily stirring.

217. **Washing, Drying, and Ornamenting Silver-Plated Articles.**—Articles that have been plated with silver are always washed in abundance of water until every trace of the depositing liquid is removed from them; they are then immersed in hot dry sawdust, moved about in it and gently rubbed with it, until they are perfectly dry. After drying they are, if necessary, weighed, to ascertain how much silver has been put upon them, then "scratched" (§ 80), if necessary, and finally finished by burnishing, polishing, &c.

Sometimes for the purpose of ornament, portions of their surface are "oxidized." This is done by applying a hot solution of bichloride of platinum (§ 167) to them, and allowing it to dry. The more platinum the solution contains, and the hotter it is, the deeper black does it produce; or it may be effected by the application of a solution of "liver of sulphur." To produce a brownish colour, apply a solution of equal weights of sulphate of copper and sal-ammoniac in vinegar; and to produce a "dead" appearance, like frosted silver, deposit a mere trace of copper upon it in a copper solution, then well wash it, and deposit a very thin layer of silver upon this. In each of these cases the parts which are to remain bright must be stopped-off with varnish.

218. **"Stripping" Silver from Copper, and Copper from Silver.**—Occasionally the depositor has sent to him, to be re-plated, old worn out articles formed of "Sheffield plate," in which the outer layer of

silver has been worn away, and exposed portions of the copper base beneath; these articles generally require to have the remaining portions of silver removed, in order to obtain a uniform surface to deposit upon. The removal of the silver is termed "stripping." To effect this, add a little nitrate of potash (saltpetre) to a quantity of strong oil of vitriol, and apply heat, until it is all dissolved; then immerse the articles in the hot liquid, and allow them to remain until all the silver is dissolved. If the action becomes slow, apply more heat or add more saltpetre; the copper will not be much acted upon if the articles are not allowed to remain in too long. A number of such articles are generally done together, and are afterwards washed, and prepared in the usual manner for receiving a deposit. The silver may be recovered from the liquid, in the form of chloride of silver, by diluting it with much water, then adding a solution of common salt to it as long as a precipitate is produced; the precipitate when washed and dried is chloride of silver. By fusing this with carbonate of potash the metallic silver is obtained.

To remove copper from silver (which is but rarely required), boil it in dilute hydrochloric acid, or immerse it in a hot solution of perchloride of iron. The latter solution may be made by digesting peroxide of iron (jeweller's rouge) in warm hydrochloric acid as long as it will dissolve; it will remove either tin, lead, or copper, from gold or silver, without affecting those metals. A solution of chloride of zinc has been used for the same purpose. Copper may also be completely removed from silver or gold, by making it the anode in a sulphate of copper solution until all the copper is dissolved; the silver will remain unaffected if the current employed is feeble and has not a greater E.M.F. than 1 or 2 pairs.

219. *Testing the Purity of Silver.*—M. Runge adopts the following method of testing the purity of silver:—He immerses the article in a mixture of 32 parts of water, 4 parts of sulphuric acid, and 3 parts of chromate of potash. If pure metal, the immersed part quickly assumes a purple colour, which is less deep and less lively in proportion to the amount of alloy contained in the silver. No other metal exhibits the same colour with this liquid.

220. *Testing the Amount of Silver and of Free Cyanide in Silver Solutions.*—To ascertain the amount of silver in a cyanide plating solution, add dilute hydrochloric acid to a known quantity of the liquid as long as it produces a precipitate; wash, dry, and weigh the precipitate, which is chloride of silver, containing in every 143·6 parts 108 parts of metallic silver. To test the amount of *free* cyanide of potassium, add a solution of crystallized nitrate of silver in distilled water to a known quantity of the plating liquid, as long as the precipitate formed is entirely re-dissolved on stirring, and note how much nitrate is used;

every 175 parts expended indicate 130 parts of free cyanide, or about 3 parts of free cyanide to 4 parts of nitrate of silver.

221. **Management of Gilding Solutions.**—Cyanide gilding solution is generally contained in a glazed iron vessel, and heated either by a stove or by gas jets beneath; or it is contained in a stoneware or glass pan immersed in boiling water. On account of the usual smallness of the articles to be gilded, the thinness of the deposit required, and the rapidity of the action in a hot liquid, the articles only require to be immersed in the solution for a few minutes; when a thicker deposit is required, they should be taken out several times, brushed, and re-immersed, in order to maintain a proper condition of deposit. Articles formed of iron or steel require to be coated with a thin film of copper in the cyanide coppering liquid before gilding. The strength of battery used for gilding is generally about 2 pairs of Smee's, of different sizes, according to the magnitude of the articles to be gilded. The loss of water by evaporation is generally made good by adding a little distilled water, after the gilding is finished.

222. *Regulation of Colour in Electro-gilding.*—The general method now adopted for regulating the colour of electro-gilding is as follows:—After having prepared the solution, work it with a large copper anode until the deposited metal begins to deteriorate in colour; then replace the copper by a small gold anode. With the copper anode can be obtained a rich full colour, becoming deeper as the temperature of the liquid is higher; to produce a paler yellow, use a small gold anode with a lower temperature, or add a little caustic soda, or some cyanide of silver solution. The deposited metal is an alloy.

223. **Recovery of Gold and Silver from Depositing Liquids.**—As both silver and gold solutions occasionally get out of working condition and become quite unfit for use, it is very desirable that the operator should understand the chemical action of different substances upon them, and how to recover the metal. Those of silver generally get out of order, either from the addition of too much "brightening liquid;" from excess of cyanide of potassium, together with the heat of the weather, and injudicious management; from unsuccessful attempts to improve the condition of the liquid; from the accidental introduction of impurities; or from the liquid having been improperly made. Supposing it to be the usual cyanide liquid, the silver may be recovered in the metallic state thus:—Evaporate the solution to dryness, reduce the resulting salt to powder, mix it with its own weight of a mixture of ½ part of nitrate of potash and 2 parts of common salt, and roast the whole in an iron pan to dryness. Fuse the dried mixture at a bright red heat in an earthen crucible, until the liquid silver collects at the bottom of the vessel, then pour the silver only slowly into a large quantity of water. The resulting granules

of silver should not be used in making a new plating liquid, because they generally contain copper derived from the articles suspended in the plating solution (§153 and §233), but should be exchanged at a silver refiner's for pure silver.

224. "The crystallized double cyanide of gold and potassium fuses and effervesces by heat, and is resolved into cyanogen gas, ammonia, and cyanide of potassium, if air be present; its complete decomposition requires a strong red heat. When it is mixed with an equal weight of carbonate of potash and strongly heated, a button of metallic gold is obtained. When heated with sulphuric acid, it gives off hydrocyanic acid gas, and, after ignition, leaves a mixture of gold and sulphate of potash. Iodine sets free cyanogen gas, forms iodide of potassium, and throws down the cyanide of gold. The aqueous solution of cyanide of gold and potassium gilding liquid, when mixed with sulphuric, hydrochloric, or nitric acid, slowly deposits cyanide of gold; and when boiled with hydrochloric acid, it is completely resolved into cyanide of gold and chloride of potassium. Similar effects are produced even by oxalic, tartaric, and acetic acid."

225. *Extraction of Gold and Silver from Exhausted Solutions.*—"To obtain the remaining gold from gilding solutions which have become inactive, they should be evaporated to dryness, the residue finely powdered and intimately mixed with an equal weight of litharge, fused at a strong red heat, and the lead extracted from the alloy button of gold and lead by warm nitric acid; the gold will then remain as a loose yellowish-brown spongy mass."—Bœttger, J. Pr. Chem. 36, 169. Elsner, Redtel Hessenberg, J. Pr. Chem. 37, 477, 38, 169, and 256.

226. The following extracts are from a paper by Elsner:—"I have undertaken a series of researches upon this object, and hasten to communicate the results to the public; but, before proceeding to the communication, I think it necessary to mention the results of the experiments upon which are based the methods given further on for extracting both the silver and the gold of old cyanide of potassium liquids.

227. "1st. If we add hydrochloric acid to a solution of silver in cyanide of potassium, until the liquid exhibits an acid reaction, we obtain a white precipitate of chloride of silver, which, when submitted to heat, melts into a yellow mass. If this was cyanide of silver, the application of a red heat would have left a regulus of silver. The addition of the hydrochloric acid precipitates all the silver present in the liquid in the form of chloride of silver.

228. "2nd. If we evaporate a solution of silver in cyanide of potassium to dryness, and heat the residue to redness until the mass is in a state of quite fusion, and has assumed a brown colour, there remains,

when we wash the mass with water, metallic and porous silver. The wash-waters, when filtered, still contain a little silver in solution; because, if hydrochloric acid is added to them, it produces a precipitate of chloride of silver. In evaporating and calcining a solution of gold in cyanide of potassium the result is the same—we obtain metallic gold. The wash-waters, acidulated with hydrochloric acid, give, when treated with sulphuretted hydrogen, a brown precipitate of sulphide of gold; and, with chloride of tin, a violet precipitate (purple of Cassius)—a proof that these liquids still contain a little gold in solution.

229. "3rd. If we pour upon finely-divided silver—for instance, silver-leaf, or silver precipitated in the porous state by zinc from a solution of silver—a concentrated solution of cyanide of potassium, at the ordinary temperature, and shake it frequently, the liquid, at the end of a certain time, exhibits silver in solution, and, by adding hydrochloric acid to it, we produce an abundant precipitate of chloride of silver. This experiment explains why, in the wash-waters of the various combinations of gold or silver with cyanide of potassium, we can still demonstrate the presence of gold and of silver after the most minute separation.

230. "4th. When hydrochloric acid or ordinary sulphuric acid is added to a solution of cyanide of copper and cyanide of potassium, until the liquid exhibits an acid reaction, there results a reddish-white precipitate, which is a cyanide of copper in the anhydrous state. If the precipitate be well washed and boiled in potash lye, protoxide of copper is separated of a beautiful red colour; and if to the filtered alkaline liquid we add a solution of green copperas, a dirty blue precipitate is obtained. A solution of carbonate of soda furnishes the same results, and yields, with the copperas, the same dirty blue precipitate. If the reddish-white precipitate is dissolved in pure nitric acid, and a solution of nitrate of silver added to it, an abundant white precipitate is produced, which, when washed, dried, and calcined, yields silver in the metallic state—a proof that the precipitate is cyanide of silver.

231. "The reddish-white precipitate is soluble in an excess of hydrochloric acid, in nitric acid, and in aqua regia; it is also soluble in aqueous ammonia, and in a solution of cyanide of potassium." The "reddish-white precipitate" spoken of by Elsner appears to be the same as that which is precipitated by strong acids from old silver plating liquids containing much copper, &c., dissolved from the articles during plating, and from the copper connecting wires; and consists of cyanide of silver coloured by cyanide of copper and other impurities.

232. "5th. If we pour hydrochloric acid into a very pure solution of gold in cyanide of potassium, there is slowly formed at ordinary *tem*peratures, and immediately on the application of heat, a yellow

precipitate, which is cyanide of gold; the filtered liquid which has given this precipitate still contains a little gold in solution. By evaporating it to dryness, fusing, dissolving, and filtering again, there remains upon the filter the remainder of the gold.

233. "When a solution of silver prepared for silvering articles of bronze or of brass has been employed a certain time for that purpose, the precipitate produced in it by the addition of hydrochloric acid is not pure white but reddish, in consequence of the reddish-white cyanide of copper which is precipitated with it; for we know that those silvering liquids which have been used for some time contain copper in solution. The same thing occurs with the solutions for gilding, in which articles of silver, copper, bronze, and brass have been gilded for a long time; the liquid contains, after a certain time of service, not only gold, but also silver and copper. This case presents itself especially when gilded articles of silver, containing copper or other alloys of silver, are in the solution of gold; then the precipitate of cyanide of gold produced by the addition of hydrochloric acid does not possess its proper pure yellow colour. It has happened to me to observe a precipitate of this kind, which, instead of being yellow, was green; and, in fact, articles of iron have been gilded in the solution, and the precipitate contained, besides cyanide of gold, Prussian blue, so as to be demonstrated in an examination, which consisted in boiling the green precipitate in aqua regia, filtering to separate the dirty green residue, evaporating the filtered liquid to dryness, and dissolving the dry salt in water acidulated with hydrochloric acid; the addition of sulphate of iron to this new liquid gave a brown precipitate, and the salts of tin a reddish-brown precipitate. In treating by aqua regia, the cyanide of gold was then decomposed, and converted into chloride of gold.

234. "Based upon the preceding facts we may found several methods for recovering all the silver and gold of old cyanide of potassium solutions. The extraction of these precious metals may be effected either by the wet or by the dry process.

235. "*Extraction of Silver by the Wet Method.*—Adding hydrochloric acid until the liquid exhibits a strongly acid reaction (§ 230). The precipitate of chloride of silver which is thus obtained will be, as we have already said, of a reddish-white colour, because of the cyanide of copper which is precipitated with it when the solution has been used a long time for silvering objects containing copper. In this precipitation by hydrochloric acid there is hydrocyanic acid gas set free; therefore the operation should only be performed in the open air, or in a place where there is good ventilation. If the precipitate is very red it must be treated with hot hydrochloric acid, which will dissolve the cyanide of copper. The chloride of silver, having been washed with

water, must be dried, and then fused with potash in a Hessian crucible, coated with borax, in the ordinary manner for obtaining metallic silver.

236. "This method is very simple in its application, and very economical, considering that by the aid of the hydrochloric acid all the silver contained in the solution of cyanide of potassium is precipitated, and there remains no trace of it in the liquid. But the large quantity of hydrocyanic acid gas which is disengaged is a circumstance which must be taken into serious consideration when operating on large quantities of silver solution, the vapour of which is most deleterious, and nothing but the most perfect ventilation, combined with arrangements for the escape of the poisonous gases, will admit of the process being carried on without danger to the workmen; when, however, we have taken the precautions dictated by prudence, the method in question may be considered as perfectly practical. The liquid should be poured into very capacious vessels, because the addition of the acid produces a large amount of froth.

237. "*Extraction of Silver by the Dry Method.*—The solution of cyanide of silver and potassium is evaporated to dryness, the residue fused at a red heat, and the resulting mass, when cold, is washed with water. The remainder is the silver in a porous metallic condition. There still remains in the wash-waters a little silver, which may be precipitated by the addition of hydrochloric acid.

238. "*Extraction of Gold by the Wet Method.*—A solution of gold and cyanide of potassium, which has long served for gilding articles of silver alloyed with copper, may still contain, as we have already remarked, independently of the gold, both silver and copper, and perhaps iron. In order to obtain these metals we operate in the following manner:—

"The liquid, the same as with the solution of silver, is acidulated with hydrochloric acid; in which case there is produced a disengagement of hydrocyanic acid gas, which requires the same careful ventilation. This addition of hydrochloric acid causes a precipitate, which may, according to circumstances, consist of cyanide of gold, cyanide of copper, and chloride of silver. The precipitate, washed and dried, is boiled in aqua regia, which dissolves the gold and copper in the form of metallic chlorides, and leaves the chloride of silver unaffected. The solution, containing the gold and the copper, is evaporated nearly to dryness in order to drive off any excess of acid; it is then dissolved in a small quantity of water, and the gold precipitated from it, in the state of a brown powder, by the addition of protosulphate of iron. The chloride of silver is reduced to the metallic state by the known means. The liquid from which we have precipitated the cyanide of gold, &c., by hydrochloric acid, may yet contain a little gold in solution. *I refer to* "5th" for its further treatment.

239. "This method is distinguished by the great simplicity of the operation, and we may repeat for it all that we have already said respecting the extraction of silver by the wet method.

240. "*Extraction of Gold by the Dry Method.*—The solution of cyanide of potassium which contains gold, silver, and copper, is evaporated to dryness; the residue fused at a red heat, cooled and washed (the wash-waters still contain a little gold and silver, and this occurs most often when the solution of gold or silver contains a very great excess of cyanide of potassium). The residue, after washing, consists of gold and silver in a metallic porous state, and carbide of copper resulting from the decomposition of cyanide of copper by the heat. The metallic residue is treated by aqua regia, which forms insoluble chloride of silver, and contains the chlorides of gold and copper in solution. In order to obtain these metals in the metallic state we must proceed in the manner previously indicated.

241. "If we operate according to the method of Professor Bœttger, *i.e.*, if we fuse the dried residue with its own litharge, in a covered crucible, the regulus we obtain in this case consists of gold, silver, and lead. In treating this alloy by nitric acid of specific gravity 1·2, and applying heat, the gold remains in the form of a brown powder, whilst the lead and the silver are dissolved in the acid. This solution, after having been diluted with distilled water, may have the silver separated from the lead, by the addition of hydrochloric acid.

242. "These methods of extracting the silver and gold from old solutions of cyanide of potassium by the dry process, present this advantage, that the operator is not incommoded, while working, by the disengagement of vapours of hydrocyanic acid. In these operations the poisonous gases are not developed as they are in the processes for extracting the metals by the wet process.

243. "After the experiments here reported, those who are interested in the subject may choose for themselves which of these methods appear the most suitable to the circumstances in which they are placed, and the object which they wish to attain.

244. "*Means of Recovering Gold or Silver, by M. Bolley.*—Cyanide of gold dissolved in an excess of cyanide of potassium resists all the means which we have tried to separate them; and hydrosulphuric acid, for example, does not produce a precipitate. By the wet method we cannot always precipitate the gold completely, and for that reason MM. Bœttger, Hessenberg, Elsner, and others, propose to evaporate the liquid to dryness; mix the residue with its own weight of litharge, fuse the mixture at a strong red heat, then dissolve the lead from the alloy by boiling it a long time with dilute nitric acid, which leaves the gold in the form of a light sponge.

245. "M. Wimmer has more recently proposed to evaporate the

solution to dryness in a water bath, then mix the residue with one and a-half times its weight of saltpetre, and introduce the mixture by small portions at a time into a Hessian crucible, heated to redness in order to cause explosions, and to continue this until the entire mass is in a state of quite fusion.

246. "The first of these two processes does not give room for any objection, except in the employment of a great heat, and the use of nitric acid; the second process is, on the contrary, disagreeable, and very uncertain. We know that saltpetre never explodes with more violence than with cyanide of potassium; and, nothwithstanding that the inventor of the process advises us not to add more than small portions of the mixture at a time, the explosions are so powerful that they cannot be caused without loss of materials.

247. "The following process is applicable on the small scale with a spirit lamp and a crucibile of platinum:—Evaporate the solution to dryness, mix the saline mass with its own weight of sal-ammoniac, and heat it gently; ammoniacal salts decompose, as we have said, the metallic cyanides, and form cyanide of ammonia, which is itself decomposed by the heat and volatilized, whilst the acid of the ammoniacal salts (the body which salifies the ammonia) combines with the metals (passed to the state of the oxides) which were previously united to the cyanogen. The sal ammoniac then in this case forms chloride of potassium and chloride of gold, and, if the salt contains ferrocyanide of potassium, chloride of iron in addition. The chloride of gold is easily decomposed; the chloride of iron is partly decomposed, and leaves oxide of iron in beautiful crystalline spangles. The undecomposed portion of the chloride of iron, like the chloride of potassium, may, after the decomposition is finished (which only requires a low red heat), be washed away by water, leaving the gold in the form of a light coherent mass, and the iron in small spangles, which may be removed by mechanical means.

248. "If we fear that a little of the gold remains mixed with the iron in a pulverulent state, we may dissolve it in hot aqua regia, and precipitate the gold from the resulting solution by adding to it a solution of protosulphate of iron; but this appears superfluous, and I am assured, by evaporation of given volumes of the same solution of gold, the evaporation and calcination of the sal-ammoniac, and other operations, that we have collected in a sufficiently exact manner all the gold of these solutions.

249. "The same process is applicable to the solution of silver; and, independently of the oxide of iron (of the ferrocyanide of potassium), we obtain chloride of silver, which is soluble in aqueous ammonia."

Table of Corresponding Temperatures of Centigrade and Fahrenheit Thermometers.

Deg. Cent.	Deg. Fahr.	Deg. Cent.	Deg. Fahr.	Deg. Cent.	Deg. Fahr.
100	212·	66	150·8	32	89·6
99	210·2	65	149·	31	87·8
98	208·4	64	147·2	30	86·
97	206·6	63	145·4	29	84·2
96	204·8	62	143·6	28	82·4
95	203·	61	141·8	27	80·6
94	201·2	60	140·	26	78·8
93	199·4	59	138·2	25	77·
92	197·6	58	136·4	24	75·2
91	195·8	57	134·6	23	73·4
90	196·	56	132·8	22	71·6
89	195·2	55	131·	21	69·8
88	190·4	54	129·2	20	68·
87	188·6	53	127·4	19	66·2
86	186·8	52	125·6	18	64·4
85	185·	51	123·8	17	62·6
84	183·2	50	122·	16	60·8
83	181·4	49	120·2	15	59·
82	179·6	48	118·4	14	57·2
81	177·8	47	116·6	13	55·4
80	176·	46	114·8	12	53·6
79	174·2	45	113·	11	51·8
78	172·4	44	111·2	10	50·
77	170·6	43	109·4	9	48·2
76	168·8	42	107·6	8	46·4
75	167·	41	105·8	7	44·6
74	165·2	40	104·	6	42·8
73	163·4	39	102·2	5	41·
72	161·6	38	100·4	4	39·2
71	159·8	37	98·6	3	37·4
70	158·	36	96·8	2	35·6
69	156·2	35	95·	1	33·8
68	154·4	34	93·2	0	32·
67	152·6	33	91·4		

Numerical Relations of Thermometric Scales.

9 Fahrenheit degrees equal 5 Centigrade degrees, or 4 Reaumur degrees.

To convert—								
Fahr. to Cent. ...	subtract ...	32	multiply by ...	5	and divide by	9
,, ,, Reaumur ...	,, ...	32	,, ,, ...	4	,, ,, ,,	9
Cent. to Fahr. ...	multiply by	9	divide by ...	5	and add ...	32
,, ,, Reaumur ...	,, ,,	4	and divide by	5		
Reaumur to Fahr. ...	,, ,,	9	,, ,,	4	and add ...	32
,, ,, Cent. ...	,, ,,	5	and ,, ,,	4		

Example to convert 212 Fahr. to Centigrade ...

212
32
180
5
9)900
100 Cent.

Table of Useful Numerical Data.

1 millimetre equals...	·03937	inches.	
1 centimetre ,, ...	·39370	,,	
1 decimetre ,, ...	3·93700	,,	
1 mitre ,, ...	39·37000	,,	
1 cubic centimetre of water equals	1·	gramme.	
1 litre ,, ...	1000·	,,	
1 litre ,,	35·275	ounces by measure.	
1 gallon (or 160 fluid ounces) equals	4·536	litres.	
1 gallon ,, ...	277·276	cubic ins.	
1 pint (or 20 fluid ounces) equals	34·659	,,	
1 fluid ounce ,, ...	1·733	,,	
1 litre ,, ...	61·024	,,	
1 avoirdupois pound equals	7000·	grains.	
1 troy pound equals...	5760·	grains.	
1 avoirdupois ounce equals	437·5	,,	
1 troy ounce ,, ...	480·	,,	
1 avoirdupois drm equals	27·34	,,	
1 troy pennyweight equals	24·	,,	
1 gramme ,, ...	15·43	,,	
1 kilogramme ,, ...	15432·	,,	
1 litre of water ,, ...	15432·	,,	
1 cubic inch of water equals	252·5	,,	
1 cubic centimetre of water equals	1·	gramme.	
1 kilogramme ,,	35·274	avoirdupois ozs.	

Table of Electric Conducting-Powers of Metals (Mathieson).

	Conducting-powers.		Conducting-powers.
Silver	100·	Tin	12·4
Copper	99·9	Thallium	9·2
Gold	77·9	Lead	8·3
Zinc	29·0	Arsenic	4·8
Cadmium	23·7	Antimony	4·6
Platinum	18·0	Mercury...	1·6
Cobalt	17·2	Bismuth	1·2
Iron	16·8	Graphite	·069
Nickel	13·1	Gas Coke	·038

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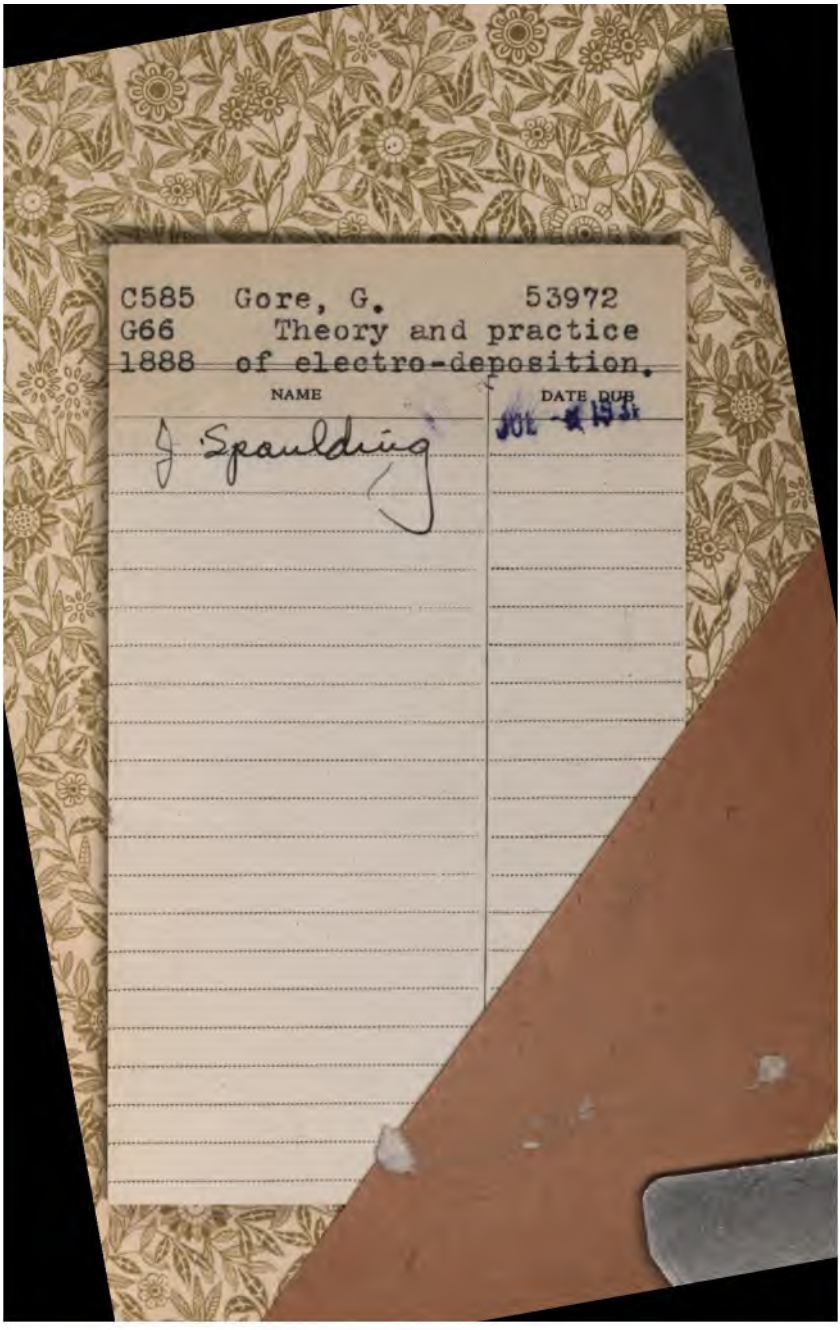

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